Examination for the Associateship (A.S.D.C.) 1959

The sixth examination for the Associateship of the Society of Dyers and Colourists was held in June 1959, and below appear the question papers and the report of the Examinations Board. It is hoped that publication of these papers and the report will be helpful both to prospective candidates and to teachers, and that it will serve to inform members of the Society and others of the standard of knowledge expected from candidates for the Associateship.

Examination Papers

Papers A and B are taken by all candidates; but Papers C, D, and E are taken by a candidate only in his chosen branch of tinctorial technology. Further, in Paper E a candidate has a choice of subject— analytical and testing techniques or the organisation of production and economics

Paper A
General Chemistry and Properties of Dyes, Pigments, Auxiliary Products
General Chemistry and Properties of Organic High Polymers

10 a.m.–1 p.m. on Thursday, 4th June 1959

(SIX questions only to be attempted, three from each section of the paper)

SECTION I

1. Give an account of the chemistry of the recently introduced types of reactive dyes which combine chemically with cellulose.

2. Into what three main types may surface-active agents used in the textile industry be classified? Give examples of each type and discuss the relationship between constitution and properties.

3. Describe the principles involved and the methods employed for preparing stabilised diazo compounds for use in textile dyeing and printing.

4. What general methods are available for the introduction of the amino group into the aromatic nucleus? Give typical examples in the benzene, naphthalene, and anthraquinone series.

5. Describe the essential features which a dye molecule should possess to enable it to form a complex with a metal. Give examples of the types of metal complexes which are commonly applied to textile fibres.

6. Discuss the chemistry of reduction processes used (*a*) in preparing an intermediate for dye manufacture, **and** (*b*) for decolourising dyed textiles.

7. Starting from anthraquinone, outline the essential stages in the preparation of (*a*) an acid dye, (*b*) a mordant dye, **and** (*c*) a vat dye.

8. Give an account of the preparation and properties of **either** a phthalocyanine pigment **or** a triphenylmethane dye.

SECTION II

9. Write explanatory notes on **four** of the following—

   (*a*) Radical chain polymerisation

   (*b*) Gel point

   (*c*) Graft copolymer

   (*d*) Polyfunctionality

   (*e*) Anionic polymerisation

   (*f*) Chain transfer.

10. Outline the information that may be obtained from **either** X-ray diffraction studies **or** infrared absorption studies of high polymers.

11. (*a*) The relationship between the intrinsic viscosity $[\eta]$ and the molecular weight M of polyvinyl acetate in acetone at 25°c. is—

$$[\eta] = 1 \cdot 76 \times 10^{-4} M^{0 \cdot 68}$$

The intrinsic viscosity of a fraction of polyvinyl acetate in acetone at 25°c. was 0·65. Calculate the molecular weight of the fraction.

(*b*) Of 100 chain molecules of a polymer 10 have each a molecular weight of 100,000, 40 have each a molecule weight of 50,000, and the remaining 50 have each a molecular weight of 10,000. Calculate the number-average and the weight-average molecular weights of the polymer.

12. Discuss the effects of crystallinity and orientation on the properties of high polymers.

13. Give an account of the preparation and properties of **one** of the following types of high polymers—

    (a) Polyesters

    (b) Vinyl polymers

    (c) Cellulose esters.

14. Write an essay on **one** of the following topics—

    (a) Stereospecific polymers

    (b) Polyelectrolytes

    (c) The effects of high-energy radiation on high polymers.

technologists produce colour matches with mixtures of dyes or pigments which are coloured greenish blue, bluish red, and yellow as primaries. Why are these colours different from those used in colorimetry? What is meant by the *colour gamut* of three dyes in admixture? Illustrate your answer on a chromaticity diagram.

4. Write an essay on **one** of the following topics—

    (a) The Munsell colour system and its uses

    (b) The practical uses of instrumental colorimetry

    (c) The C.I.E. system of colour specification.

5. Define *isosbestic wavelength*.

Two dyes A and B having optical densities as shown in Table I are applied to a fabric from a

TABLE I

Wavelength, mμ.	400	430	460	490	520	550	580	610	640	670	700
A (0·3 g./litre)	0·500	0·890	1·050	1·010	0·810	0·570	0·420	0·310	0·230	0·180	0·150
B (0·1 g./litre)	0·034	0·067	0·126	0·194	0·270	0·365	0·420	0·410	0·265	0·140	0·084
Dyebath—											
0 min.	0·534	0·957	1·176	1·204	1·080	0·935	0·840	0·720	0·495	0·320	0·234
5 min.	0·393	0·703	0·855	0·859	0·748	0·617	0·534	0·445	0·318	0·208	0·156
10 min.	0·304	0·545	0·660	0·657	0·564	0·454	0·384	0·317	0·222	0·152	0·116
20 min.	0·188	0·337	0·405	0·401	0·340	0·267	0·221	0·180	0·126	0·088	0·068
30 min.	0·120	0·214	0·258	0·255	0·217	0·170	0·142	0·113	0·081	0·056	0·044
40 min.	0·083	0·149	0·181	0·181	0·157	0·128	0·109	0·091	0·064	0·043	0·032
60 min.	0·070	0·125	0·153	0·154	0·135	0·113	0·098	0·082	0·058	0·038	0·028

Paper B

Theories of Colour
Relation of Colour to Constitution
Colour Assessment and Colour Fastness

2–5 p.m. on Thursday, 4th June 1959

(*FIVE questions only to be attempted*)

1. State what types of physical instruments are, in your opinion, most suitable for the following uses, giving reasons for your choice—

    (a) Accurate measurement of small differences of colour between patterns of dyed or pigmented material

    (b) Calculation of absolute C.I.E. tristimulus values

    (c) Measurement of the extinction coefficients of dyes, and quantitative analysis of dye mixtures, in solution.

2. What do you understand by any **three** of the following—

    (a) Metameric colour match

    (b) Lambert's law

    (c) Dominant wavelength

    (d) Uniform chromaticity diagram

    (e) Specular reflection?

Illustrate your answers with diagrams where necessary.

3. Colour matches with a visual colorimeter are made by mixing three primary light sources, coloured red, green, and blue. Dyers and pigment

common dyebath, with initial concentrations 0·3 g. of A and 0·1 g. of B per litre.

Small samples of the dyebath are removed at the times shown, up to equilibrium, which is achieved in 60 min. The samples are analysed with a spectrophotometer, with the results shown in Table I. Assuming that Beer's law is obeyed by the dyes, calculate the time taken by the fabric to achieve half of its equilibrium uptake of dye. Note that it is not essential to calculate the rates of uptake of A and B independently.

6. What do you understand by the term *fluorescent brightening agent* in connection with textile materials and what is the mode of action of such an agent?

A poor-quality fluorescent brightening agent possessing blue fluorescence is applied to bleached cotton fabric at several concentrations, and the resulting patterns are measured on a three-filter photoelectric colorimeter of conventional design using Illuminant B (chromaticity $x = 0.349$, $y = 0.352$). The recorded chromaticity coefficients and luminances are shown in Table II. Visual assess-

TABLE II

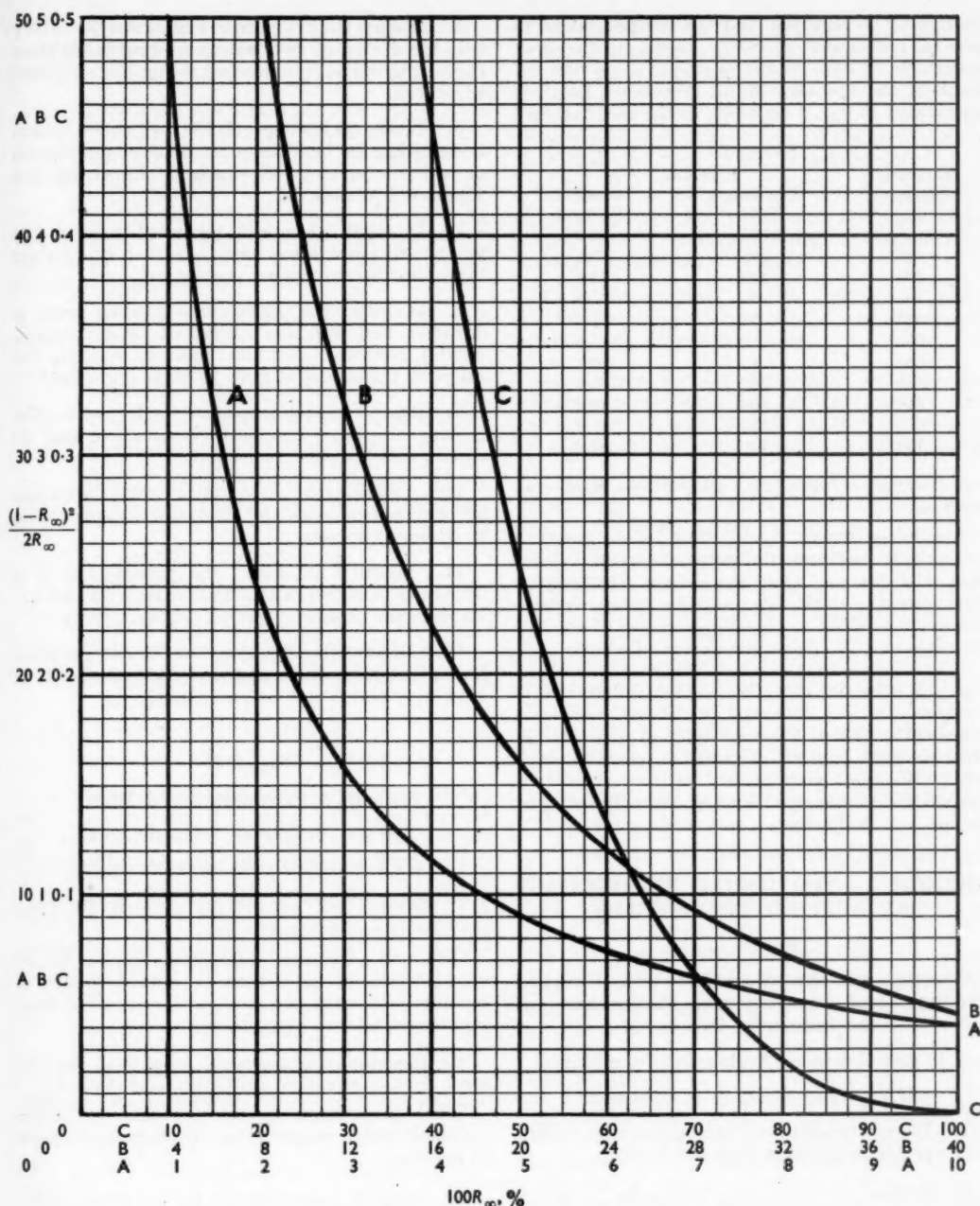| Pattern No.	Concn. of Agent (%)	x	y	Y (%)
1	0	0·370	0·367	81·0
2	0·01	0·378	0·374	80·5
3	0·02	0·388	0·382	79·0
4	0·04	0·402	0·393	76·8
5	0·08	0·414	0·402	72·4
6	0·15	0·421	0·410	66·9

FIG. 1 — Plot of Kubelka–Munk Function against Reflectance

ment of the patterns in daylight corresponding to Illuminant B shows pattern 3 to be the best white of the series. Comment on the consistency or otherwise of this result with the instrumental data. Graph paper may be used in answering the question.

7. How is the reflection of light by a very thick pad of a textile fabric related to the concentration of dye in the fibres?

A dyed textile pattern supplied by a customer of your firm is measured on a spectrophotometer and found to have the reflectances shown in Table III. What is the colour of the pattern?

It is known that the dye on the pattern is the same as that on a reference pattern in your possession which contains 0·025% by weight of dye and has the reflectances shown in Table III. Assuming the Kubelka–Munk equation to be obeyed, the absorption of light by the fibre and

the dye to be additive, and the undyed fabric to have a reflectance of 85%, calculate the concentration of dye on the customer's pattern. (A graph of the Kubelka–Munk reflectance function is provided in Fig. 1 to assist in the calculations.)

TABLE III

Wavelength (mμ.)	Reflectance (%) Customer's Pattern	Reflectance (%) Reference Pattern
400	19·9	72·3
430	25·5	75·4
460	22·2	73·7
490	9·4	61·3
520	5·2	51·8
550	4·4	48·5
580	8·9	60·4
610	25·3	75·3
640	50·0	82·2
670	63·2	83·9
700	74·6	84·6

8. Define *chromophore, auxochrome,* **and** *conjugation.*

A cellulose acetate dyeing of a yellow monoazo dye quickly loses much of its colour when illuminated with intense light, the colour returning on storage in the dark. Account for this reversible change in relation to the configuration of the dye molecule and the electronic theory of colour.

9. A colourist describes colour differences in terms of strength, hue, and brightness, whereas a colorimeter records them in terms of x, y, and Y. How are these two sets of variables related to each other? Illustrate your answer with reference to a sample of a purple dye which is markedly stronger, redder, and duller than a standard purple dye.

BRANCH 1— TINCTORIAL TECHNOLOGY AS APPLIED TO TEXTILES

Paper C

Properties of the Materials and Finished Products and Fundamental Mechanisms of the Industrial Processes

10 a.m.–1 p.m. on Friday, 5th June 1959

(*SIX questions only to be attempted*)

1. Discuss the physicochemical principles which may operate in printing with vat dyes.

2. **Either** (*a*) discuss the principles on which emulsion thickeners are formulated and used **or** (*b*) indicate how you would evaluate the flow properties of a thickening agent.

3. Give examples of dyes which are synthesised on the fibre, and outline the chemistry of each process.

4. What do you understand by *substantivity* in relation to the colouring of cellulosic fibres? Give examples from industrial processes of the need for different degrees of substantivity, and discuss the reasons for such differences.

5. Discuss the evidence in support of the theory that the dyeing of wool with acid dyes takes place through chemical combination rather than physical adsorption.

6. Write an account of the principles underlying **either** (*a*) high-temperature dyeing processes **or** (*b*) the dyeing of synthetic fibres by the Thermosol process.

7. In what ways and for what reasons has polyacrylonitrile fibre been modified to produce fibres of different dyeing properties?

8. Indicate the difference between *rate of diffusion* and *diffusion coefficient*. What experimental methods have been used to measure the diffusion coefficient of dyes in fibres and films?

9. How do metal-complex dyes for wool differ in respect of (*a*) chemical constitution **and** (*b*) dyeing and fastness properties?

10. Define the Langmuir and Freundlich adsorption isotherms and discuss their application to dyeing processes.

11. Describe in detail the preparation of a developer bath from a Fast Colour Base and its use. Explain the chemistry underlying each step.

12. Discuss the chemistry of "burnt gas fume fading" in relation to dye and fibre composition. How may this defect be prevented?

Paper D

Industrial Procedures and Plant

2–5 p.m. on Friday, 5th June 1959

(*SIX questions only to be attempted*)

1. Discuss the advantages claimed for automatic over non-automatic jigs.

Comment on the difficulties likely to be encountered in jig-dyeing a cotton poplin a medium blue with vat dyes, and state what steps you would take to avoid them.

2. Describe the methods employed for the azoic dyeing of cotton (*a*) hanks **and** (*b*) cloth.

What precautions would you take to ensure uniform dyeing, together with adequate fastness to rubbing?

3. Describe a machine for dyeing loose wool.

Why is wool dyed in this form, what classes of dyes are used, and what are the fastness requirements of the dyed wool?

4. How would you prepare, dye, and finish an all-wool dress fabric a medium brown?

What properties are required in the dyes used for this purpose?

5. What do you understand by the term *setting* as applied to the processing of man-made fibres? Illustrate your answer with reference to **two** of the following fibres—

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(a) Nylon

(b) Terylene

(c) Cellulose triacetate.

6. Give a short account of the methods used for printing secondary cellulose acetate dress fabrics. What difficulties are likely to be encountered in handling this type of work?

7. Describe the construction of a modern jig and a modern winch machine, and state how they differ from the older types. What types of fabrics are dyed on each machine?

8. How would you prepare and dye the following fabrics—

(a) A viscose rayon staple dress fabric for subsequent resin finishing

(b) A viscose rayon warp-knitted lingerie fabric

(c) A secondary cellulose acetate dress poult?

9. Give an account of the preparation, dyeing and finishing of nylon in **one** of the following forms—

(a) Ladies' fully fashioned hose

(b) Warp-knitted fabric

(c) Woven fabric.

10. Write an essay on **one** of the following—

(a) Faults in printing, their occurrence and avoidance

(b) Discharge styles in printing

(c) Automatic screen printing machines.

11. Why is it necessary to desize before dyeing fabrics made with sized warps? What substances are commonly used for sizing cotton and viscose rayon? What methods are employed for desizing?

12. How do Orlon and Acrilan differ in dyeing behaviour?

Give a brief account of the methods used for dyeing acrylic fibres.

Paper E

10 a.m.–1 p.m. on Saturday, 6th June 1959

(**Either** Paper (i) **or** Paper (ii) to be attempted)

(i) Analytical and Testing Techniques

(*FIVE questions only to be attempted*)

1. Describe and discuss methods which have been used to assess (a) resistance to soiling **and** (b) pilling of textile materials.

2. A Jacquard fabric has a warp of continuous-filament nylon and cellulose acetate and a weft of blended wool and viscose rayon staple. State how you would identify each of these fibres, and describe the essential principles of a method of quantitative analysis of the fabric.

3. State the fastness tests you would carry out to determine the suitability of coloured fabrics for the following—

(a) Sports shirts

(b) Swimsuits

(c) Car upholstery

(d) Worsted suitings.

Give practical details of **two** of the tests— other than light fastness— which you advocate.

4. Describe the methods of ion-exchange, chromatography, and paper electrophoresis. Give an account of the application of **one** of these methods in the field of textiles.

5. Write an essay on the removal of added matter from textile materials with particular reference to analysis and testing.

6. Discuss the significance of humidity and spectral composition of the incident light in testing the fastness to light of dyed textiles by exposing (a) to daylight under glass **and** (b) in a fading lamp.

7. Give essentials of one method in each case which may be used for the quantitative determination of **three** of the following—

(a) Formaldehyde in commercial formalin

(b) Total hardness of a dyehouse water supply

(c) Active chlorine in commercial sodium hypochlorite

(d) Total copper in a dyed fabric

(e) The iodine value of a wool-processing oil.

8. Describe the Allwörden reaction, the Krais-Viertel (K.M.V.) test, **and** the urea–bisulphite test as applied in the investigation of damage to wool. Outline the chief uses and the limitations of each test.

9. Describe methods for investigating **three** of the following—

(a) The extent of suspected mildew attack on a cotton awning

(b) The uniformity of application of a crease-resist resin to a spun viscose rayon fabric

(c) The residual alkali in a sample of scoured wool

(d) The acetyl content of a cellulose acetate fabric.

10. For what types of problem might the practical dyer make use of a systematic scheme for the identification of dyes on textile fibres?

Suggest a scheme for distinguishing between direct, azoic, vat, and reactive dyes on cellulosic fibres.

11. Write notes on the following—

(a) The care and maintenance of an analytical balance

(b) The calibration of graduated glassware

(c) The statistical comparison of the effects of two treatments on a textile material.

12. What methods have been devised to assess the water-repellency of fabrics? Explain the need for various types of test method.

(ii) Organisation of Production and Economics

(SIX questions only to be attempted)

(**N.B.**— The term *finishing works* is meant to apply to any branch of bleaching, dyeing, and printing)

1. The foreman occupies a key position in the internal communications of a factory. Discuss and suggest how he should be selected and trained.

2. What do you understand by line, functional, and staff relationships in the production organisation of a medium-sized textile finishing works? Illustrate your answer with a chart.

3. What do you know about joint consultation in industry? Suggest the composition and the terms of reference of a committee.

4. Describe an ideal plant lay-out for a particular branch of dyeing or printing.

5. Discuss quality control of production, and suggest how it can be achieved in a dyeing and finishing works.

6. Write about **one** of the following—

(a) Safety committees

(b) Plant maintenance

(c) Materials handling.

7. What do you know about incentive payment schemes? Give one example.

8. Give some reasons why demand has decreased in the textile industry and suggest what action can be taken to remedy this.

9. Cost accounting is an integral part of good management. Describe the function of the costing department and the main items of cost in a textile finishing works.

10. Discuss the various production and economic aspects of batch as against continuous processing.

Report of the Examinations Board

The 1959 examination was held in the United Kingdom in Belfast, Bradford, Manchester, Nottingham, and Paisley, and overseas in Bombay (India) and Lima (Peru). This is the first time that examination centres have had to be provided outside the United Kingdom.

The annual increase in the number of candidates taking the examination was maintained, as shown by the following table—

Year	Number of Candidates	Associates Elected
1954	9	5
1955	21	9
1956	34	16
1957	39	19
1958	40	15
1959	47	17

This year, of the 47 candidates, 20 took only the theoretical papers (A, B, and C) and 11 satisfied the examiners; 12 took the examination as a whole and 8 satisfied the examiners; 12 took the papers necessary to complete the examination and 9 reached a satisfactory standard. As a result of the written examination and subsequent interview the Board recommended 17 of the candidates, whose names are given in the Appendix*, for election as Associates. One of the candidates could not complete the examination, but reached a satisfactory standard in the one paper he took.

A few candidates still present themselves a year or two before they are fully prepared. Completion of a course of studies does not necessarily imply fitness to take the examination. A candidate should weld together the knowledge gained during his academic studies with that gained in works practice. Too often these have been kept apart and little attention has been paid to knowledge acquired in the works. For instance, some candidates who in their professional life do no analysis or testing prefer to take Paper E(i),

although Paper E(ii) would be much more suitable, not only because of their existing knowledge, but because by study for it they would be better prepared for their future careers.

A regrettably large proportion of the candidates appeared to be unable to carry out simple calculations or operations with logarithms, and it will probably be necessary, in future examinations, to include more compulsory questions which call for calculations.

Compared with those of previous years, this year's candidates were often weak in their knowledge of dyeing and printing mechanisms and in the application of theory to practice.

The examiners again complained of the bad, sometimes very bad, handwriting of some candidates. Self-interest at the very least should suggest that it be made as easy as possible for the examiner to read the replies. Far too many of the candidates found difficulty in expressing themselves, in giving logical form to their answers and in indicating how reports on tests and analyses should be made. More definite training in these matters might be provided. Spelling was often so poor that even words in the questions were misspelt in the answers, which can only be attributed to carelessness and lack of powers of observation.

The Board expresses its thanks to the following authorities for providing examination centres and invigilators—

United Kingdom	The College of Technology, Belfast
	Bradford Institute of Technology
	The Manchester College of Science and Technology
	Nottingham and District Technical College
	Paisley Technical College
India	The University, Bombay
Peru	The British Examinations Centre in Peru, Lima.

In addition the Board expresses its deep appreciation of the work of the examiners.

The following remarks on the results of the individual papers include the comments of the examiners, and they should serve to guide candidates, as well as those responsible for their training, both in educational establishments and in industry. Comments by the examiners are given below in the portion inset in smaller type.

Paper A

This paper was taken by 38 candidates of whom 27 attained a satisfactory standard in both sections.

SECTION I

Several candidates reached a very high standard. In general the questions relating to dyes were answered well, but the general chemistry questions dealing with intermediates were attempted by only a few candidates. Thus Question 4 was attempted by only 7 candidates, all of whom gave unsatisfactory answers. Surprisingly, Question 2 was attempted by only 2 candidates, and the answers of both were also unsatisfactory.

SECTION II

Over one-third of the candidates seem either not to have appreciated the standard required or to have had inadequate preparation. Once again a considerable number appeared not to have understood that the paper demands knowledge of the chemistry and properties of high polymers in general and not merely of those used as fibres. It is difficult to avoid the conclusion that some courses of preparation for this paper concentrate unduly on polymers from the point of view of fibre formation and fibre properties.

Most candidates attempted Question 9 dealing with aspects of polymerisation, and showed reasonable grasp of the terms. The few who attempted Question 10 restricted themselves to X-ray diffraction, usually with rather poor results. It is surprising that no-one wrote on infrared absorption, which is, of course, very useful for identifying many chemical groups and for estimating crystallinity in polymers. Although Question 11 was attempted by exactly one-half of the candidates, only one returned correct answers to all three calculations, many not understanding how the average molecular weight could be calculated. Question 12 was also popular, being chosen by 20 candidates, but was not generally well answered. There was a tendency to consider crystallinity and orientation only when polymers are in the form of fibres. This tendency was also marked in Question 13, where accounts of polyesters were almost entirely restricted to polyethyleneglycol terephthalate. On the other hand, accounts of cellulose esters were generally good and not confined to fibre aspects. Essays dealt largely with stereospecific polymers and generally showed reasonable grasp of the principles involved.

Paper B

This paper was taken by 39 candidates, 29 of whom proved to be satisfactory. The range of knowledge displayed in the answers ranged from 1 outstanding and 3 very good sets of replies, to 2 extremely bad ones. The last were written by candidates who, in their present state of knowledge, were ill-advised to enter for the examination at all. Several candidates had obviously prepared insufficiently, as was shown either by the lack of fundamental knowledge or by the variable quality of the answers. Several candidates from the same district made the same factual mistakes, which would seem to indicate a common source of their shortcomings. A number

of candidates marred good papers by careless mistakes, whilst one who had adequate knowledge betrayed in his answers and when interviewed that he lacked confidence in himself.

The subject of this paper is one which, except for a candidate of unusual ability and determination, can be prepared for only by a systematic course of study in an adequately staffed and equipped educational establishment. Candidates who feel uncertain of their ability to cope with it would be well advised to take a further year of study before making their attempt. For instance, the paper was re-taken this year by 7 candidates who had been referred from a previous examination, and the marked, occasionally impressive, improvement shown by most of them confirms the belief that previous efforts were made too soon. Several of them remarked during the interview that the extra year of study had been most beneficial, because it enabled them to tackle this paper with much greater confidence and made clear many matters in related subjects about which their minds had formerly been rather confused.

Paper C

This paper was taken by 22 candidates, of whom 16 reached the required standard. With the exception of one very good set of replies, the knowledge displayed by the successful candidates was moderately or barely adequate. In framing some of the questions the examiners desired to test ability to apply fundamental principles to industrial processes. The results were disappointing, and much below the standard attained in previous years.

The examiners' report on the individual questions, the number of attempts at each being given in parentheses, is—

QUESTION 1 (1) AND 2 (1)— Unpopular questions.

QUESTION 3 (11)—Only 5 of the answers were satisfactory.

QUESTION 4 (15)— Candidates answered the first (theoretical) part reasonably well, but failed almost entirely to answer the second part dealing with practical applications of theory.

QUESTION 5 (13)— Not answered well by most of the candidates who chose it. The theory of wool dyeing appeared to be rather unfamiliar.

QUESTION 6 (a) (19) and (b) (1)— Most answers were good.

QUESTION 7 (17)—Answered fairly well, but most candidates failed to stress the difficulty of dyeing straight polyacrylonitrile.

QUESTION 8 (8)— Answered very poorly. Only one of the candidates who chose it revealed even barely adequate knowledge. Either Fick's equation or its application to dyeing was unknown. In many cases no indication was given of how the results of diffusion experiments enable the diffusion coefficient to be calculated.

QUESTION 9 (16)— Generally well answered. There were two outstandingly good replies.

QUESTION 10 (7)— The equations were usually known, but their application to dyeing was not very well understood, there being but one outstandingly good reply.

QUESTION 11 (9)— Good replies were received from only 4 of the candidates who attempted it. Many were ignorant of the importance of the pH of the coupling bath.

QUESTION 12 (12)— Generally well answered, especially in connection with "inhibitors". Of the candidates taking it, only 3 failed.

Paper D

This paper was taken by 23 candidates, of whom 19 proved to be satisfactory. With few exceptions the answers were at a reasonably high standard.

In his report the examiner states that—

As was the case last year, the most outstanding impression is the wide variation in the standard of answers by one and the same candidate to different questions. This specialist knowledge appears to depend on the district from which the candidate comes, and is sufficiently noticeable to warrant attention from those responsible for teaching and training in this aspect of tinctorial technology. It is essential that a candidate should have a general knowledge of dyeing and printing, as well as specialised knowledge in a particular field. Some descriptions of machines were meagre, phrases like "the usual type of hank dyeing machines can be used" should not be offered as part of an account of the dyeing of cotton hanks. During the interviews it was revealed that some candidates had felt the lack of a textbook dealing with the machines used in dyeing, printing, and ancillary processes. Ignorance of operating details was only too plainly evident in a few cases, e.g. the candidates who wrote of the post-setting of nylon hose "This former is allowed to go through an oven of the hot air type at a predetermined speed at a particular temperature". In the question dealing with modern jigs, statements of the type "Cotton piece goods can be dyed on the machine and with slight adaptation can be used for vat dyeing by evacuating the air and replacing by nitrogen or any inert gas", apart from showing the candidate's inability to express himself, betray his lack of both industrial experience and ability to think on practical lines— this being also true of the suggestion that the dye liquor should be electrically heated.

Paper E(i)

Fourteen candidates took this paper. Two very good sets of answers were returned, four were adequate and the remainder were average. There was considerable spread in the quality of answers given by most, indicating rather limited preparation for the examination. Many attempted to describe apparatus or methods of which they had no first-hand knowledge, and this was particularly noticeable in the replies to Questions 4, 7, 8, and 12. It was also obvious that many who have no experience either of analysis or testing in their work in industry regard this paper as one that can be readily prepared for by learning details of the methods by heart with no idea of ever applying them in practice. Such candidates would be better advised to prepare for Paper E(ii), the subject matter of which forms part of their working life. It is, however, pleasing to note that there has been this year a decrease in the type of candidate referred to and a corresponding increase in those who have taken Paper E(ii). The examiner reports that—

Many answers gave no clear indication of ability to express the results of analyses or tests in an effective way. Many candidates were also unable to discuss subjects logically, this being particularly marked in

the replies to Questions 5 and 12, and many rambling answers were written. On the other hand one or two candidates answered almost in lecture-note form, hardly justifiable with only 36 minutes available per question. It gives the impression that the details had been learnt by heart with little appreciation of the underlying principles.

QUESTION 1 (1)— The only answer was fairly good, but went little beyond brief descriptions of the test methods.

QUESTION 2 (10)— Of the 10 answers 2 or 3 were very good and the others average. A number of incorrect statements were made about the appearance or behaviour of individual fibres and the results of the quantitative analysis were often carelessly expressed.

QUESTION 3 (10)— The candidates who replied to this question answered the first part well, and, although fastness requirements were not specifically asked for, they were correctly given by several. It was not apparent from some of the answers to the second part of the question that precise details for carrying out colour fastness tests have been widely publicised by the Society. It seems too that the amendments to the *Third Report of the Fastness Tests Co-ordinating Committee*, published in January 1958, which affected some of the tests dealt with by the candidates, had gone unread.

QUESTION 4 (2)— The candidates who attempted this question gave very disappointing answers. One failed to mention paper electrophoresis, and neither candidate seemed to understand the principles of ion-exchange.

QUESTION 5 (6)— Only one answer was good, and even this, like the others, showed little indication of a systematic approach to the question.

QUESTION 6 (1)— The only candidate to choose this question gave a satisfactory answer which showed understanding of recently published work.

QUESTION 7 (7)— This question evoked some of the best answers given in the entire paper. General principles and experimental details were adequately covered, but several mistakes were made in the chemical equations and in the methods of expressing the results of the analysis.

QUESTION 8 (10)— Of the candidates replying to this question, very few showed any real appreciation of the use of the tests or of recently published work in this field. Four of the answers were rather poor.

QUESTION 9 (4)— The candidates who answered it did fairly well, but only rarely did descriptions of experimental methods reveal direct familiarity with them.

QUESTION 10 (9)— The first part of this question brought forth some imaginative responses, and most of the identification schemes suggested could be criticised only in minor details.

QUESTION 11 (0)— This question was not attempted. Thus, once again there was complete refusal to attempt a simple question dealing with statistical methods. Parts (a) and (b) could hardly be the reason for this unanimous decision to have nothing to do with calculations.

QUESTION 12 (9)— The answers were poor, because too narrow a view of the problem was taken. Surprisingly, no candidate mentioned umbrella fabrics.

Paper E(ii)

It is pleasing that a larger proportion of the candidates chose this paper rather than E(i) this year. The general standard of the answers was high and a great improvement on that of previous years. There is no doubt that this is because

greater attention is being paid to the subject matter of this paper in some of our dyeing and printing schools, a development which is very welcome. The examiner reports that—

> Of the 8 candidates who took this paper, one returned excellent answers all round, and with one exception all the rest were good or very good. There was evidence that use of their textbooks and grasp of the subject was better than in previous years. All

the questions were attempted, and it is significant that Question 10 was well understood by the four candidates who answered it. Candidates should, however, bear in mind that the examiner is not seeking their personal opinions.

C. O. CLARK (*Chairman*)

R. L. ELLIOTT   J. V. SUMMERSGILL
W. PENN   H. A. TURNER
C. B. STEVENS   T. VICKERSTAFF

Proceedings of the Society

Vat Dyeing of Cotton Fabric by Pigmentation Methods

M. R. FOX and J. F. MAWSON

Meeting of the Bradford Junior Branch held at the Bradford Institute of Technology on 25th February 1959, Mr. R. S. Harding in the chair

A brief survey of practical vat pigment padding procedures is supplemented with data on the physical properties of suitable dyes. The effect of particle size on rate of reduction is discussed in relation to its practical implications, as well as factors such as colour yield, dispersion stability and migration effects during drying. The use of a new organic polyelectrolyte as a migration inhibitor is described.

INTRODUCTION

The use of vat pigment padding for cellulosic fabrics has increased considerably during the last 25 years. What is now generally termed the *pad–jig* process was originally developed as a means of obtaining well-penetrated vat dyeings on tightly constructed materials such as canvas, duck, linen furnishings, linen dress goods, drills, and poplin. There is now no doubt whatever that the pad–jig process gives results far superior to those obtained by leuco jig dyeing, and it can be stated generally that a properly handled pad–jig application more nearly approaches the quality of a woven yarn-dyed fabric than that obtained from other forms of vat piece-dyeing, with the possible exception of certain pale-shade Soledon or acid leuco dyeings. Besides showing distinct advantages over simple leuco dyeing in the matter of yarn penetration. the pad–jig process produces a more satisfactory surface appearance and greater coverage of constructional faults and fibre-affinity differences.

Since the 1940's the pigment padding process has become even more important as the basis of the more successful, high-speed, continuous vat dyeing systems, e.g. the pad–steam sequence and the pigment pad–Standfast molten metal machine reduction sequence.

Successful operation of pigment padding processes, either for non-continuous or continuous development, depends upon numerous factors. These factors are now reviewed, and supplemented by the results of recent studies which have helped to provide a better practical understanding of the process.

PRETREATMENT OF THE FABRIC

Cotton fabrics demanding use of the vat-pigment padding method for dyeing are normally those derived from tightly spun twofold, threefold or

mixed yarns, as well as densely woven and heavy-weight cloths; such fabrics are commonly susceptible to surface damage and must therefore be prepared in open-width. One or both sides of the fabric may be singed, and the operation must be carried out with special care if a "frosted" or "peppered" appearance is to be avoided in the final dyeings. Efficient desizing is essential in order to facilitate subsequent scouring, bleaching, and mercerising. Scouring may be carried out on the jig, roll-to-roll (Benteler system), in open-width kiers, or in continuous scouring and bleaching ranges. Caustic soda scours are usually employed, and where bleaching is necessary, e.g. for pale or bright shades, hypochlorite, peroxide, combined hypochlorite–peroxide or chlorite have all proved satisfactory. If mercerising or causticising is to follow, uniform drying prior to alkali treatment is necessary, particularly when low concentrations of caustic soda are to be employed.

The importance of securing uniform and efficient preparation at all stages cannot be overemphasised: maximum absorbency should be the objective. Before pigment padding the goods must be evenly dried and preferably alkali- and electrolyte-free. If the moisture, pH or electrolyte content of the cloth varies, the resulting variation in absorbency and pick-up may give rise to uneven pigment deposition during padding, which in turn will lead to final unlevelness of shade. On the other hand, drying can be too thorough, creating a surface hydrophobic effect which prevents instantaneous wetting of the fibres during pigment impregnation. It is sound practice to give the goods a conditioning air passage before dyeing. Storage on rollers at this stage is to be deprecated; lapping or plaiting is preferable. Collection of "white" goods on rollers under high tension frequently leads to lightly-dyed edges owing to excessive tension at the selvedges. Inadequately conditioned goods

may show excess moisture in the region of the selvedges.

PADDING ASSISTANTS

Large quantities of cotton cloth are pigment padded without padding assistants. This is sound practice, provided that the cloth preparation has been carried out thoroughly. However, as an insurance against faulty preparation and in order to increase pick-up and promote penetration, a padding assistant is generally used. The following properties are required—

(1) It must be capable of maintaining the dye in a state of uniform and fine dispersion throughout the life of the padding liquor, which, in continuous dyeing operations, may be as long as 8 hr.

(2) It must not cause dispersion collapse or otherwise seriously aggregate the minute dye particles during padding

(3) It must be an efficient wetting agent over a temperature range of 20–80°c.

(4) Its efficiency must be maintained over a pH range of 6–8

(5) Any frothing produced must be easily controllable.

The most commonly used agents are of the Calsolene Oil HS (ICI) or Perminal PP (ICI) type; the former is a modified highly sulphonated oil, and the latter an alkylated naphthalene sulphonate. Both these agents fulfil the above requirements, although Calsolene Oil HS can cause aggregation with certain vat dye dispersions under conditions of high temperatures and long storage. Perminal PP, therefore, is preferred in continuous dyeing, since it has only a slight effect on dispersion stability. It is more likely to produce foams, however, owing to the rapid passage of cloth through the padding trough and the forceful expression of liquor and air at the nip. Foaming is always worse with loose open fabrics containing occluded air than with smooth fabrics of dense construction. Foaming may be eliminated by using orthodox foam guards in the padding trough or by judicious use of a silicone anti-foaming agent.

PREPARATION OF THE PADDING LIQUORS

Detailed requirements concerning the physical properties essential for vat dyes designed for pigmentation systems are given later. At this stage it suffices to say that Paste Fine, finely dispersed Powder Fine or Grain brands are required. These products must be capable of wetting easily with water and of forming fine aqueous dispersions. In general, one part of Powder Fine or Grain to ten parts of water should be considered the maximum ratio for efficient working at the dispersing stage. FD Caledon Powders Fine, for example, are best sprinkled into water at 30–50°c., and stirred until a uniform dispersion is obtained. The tendency for fine powder brands to fly calls for adequate precautions to avoid contamination of textiles by aerial transport of the dust. The I.C.I. FD Disperser [1] reduces this tendency to fly while dispersions

are being prepared. SQ Caledon Grains [2] have a great advantage over fine powders in that they have little tendency to dust and fly, whilst Paste Fine brands simply require dilution with water and the question of dustiness does not arise. Paste brands, however, require more storage space, cost more to transport and are less stable than powders or Grains from the viewpoint of freezing, evaporation, settling, and drying-out on the sides of the containers. This instability may lead to inaccuracies in recipe formulation and to a modification of their originally fine physical properties. SQ Caledon Grains sink rapidly in water and require intermittent gentle stirring for periods up to 15 min.

Before diluting to the required volume, all vat dye dispersions required for pigment padding should be passed through a fine wire-mesh screen (150–200 B.S.) or a fine cloth filter in order to remove outsize particles and extraneous matter from water supplies, etc. Padding assistants, when used, should first be dissolved and well diluted before adding to the liquor at the bulking stage immediately before padding.

THE PIGMENT PADDING OPERATION

Pad–jig development [3], pad–steam reduction [4], and pad–Standfast molten metal machine reduction [5] all call for pigmentation with vat dyes as the first stage of dyeing. There are numerous types and designs of padding mangles and ancillary equipment available. The mangle must be mechanically perfect, i.e. it must give uniform impregnation of the cloth from side to side, side to centre, back to face and end to end. The padding trough should be small; 10–25 litres (2–5 gal.) is an ideal trough capacity. Small padding troughs minimise tailing or ending effects, and wastage at the end of a run is tolerable.

A constant liquor-level device in the padding trough is essential, particularly for continuous processing, and the delivery of pigment padding liquor must be uniform. The temperature of the padding process must be rigidly controlled throughout; steam-jacketed troughs are preferable to steam pipes, which may lead to local overheating. It is rarely necessary to employ temperatures above 50°c.

If the pigmented cloth is to be jig-reduced, a batching device with an efficient friction clutch, arranged to avoid tension build-up as the batch diameter increases, is essential. In continuous operation the goods are passed directly from the pigment padding stage to the hot-flue drier or, in the case of the wet-on-wet process, to the reduction unit.

PHYSICAL PROPERTIES OF VAT DYES

The advent of continuous processing, in particular, created the demand for vat dyes of vastly improved physical properties. In comparing commercial vat dyes of some twenty years ago with present-day products, most dyers will freely admit that the dyemakers have made noteworthy improvements. Fineness of particle size alone will not provide the desired properties; the production

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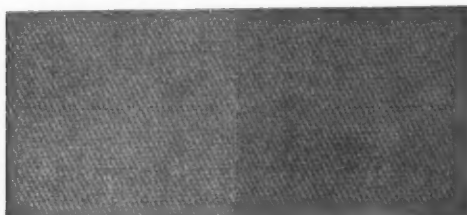entre,
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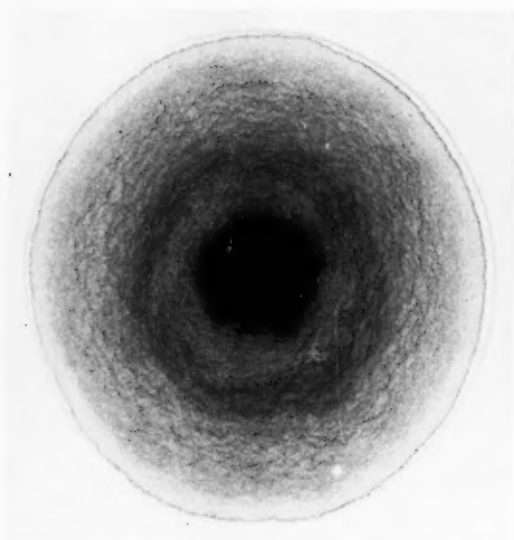

Caledon Gold Orange 3G

Caledon Brilliant Red 3B

Caledon Jade Green XBN

FIG. 1—Colour Development of Padded Vat Dyes in Standfast Molten Metal Machine:
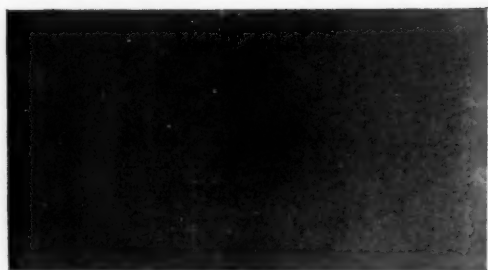Slow- and Fast-reducing Samples
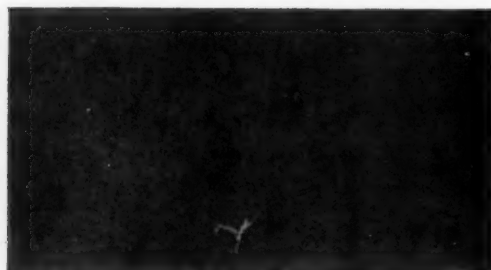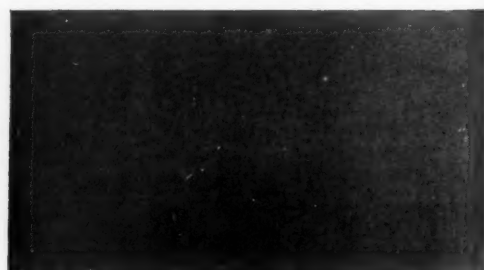
Coarse particle size

Fine particle size

Pad–Steam

Pad–Steam
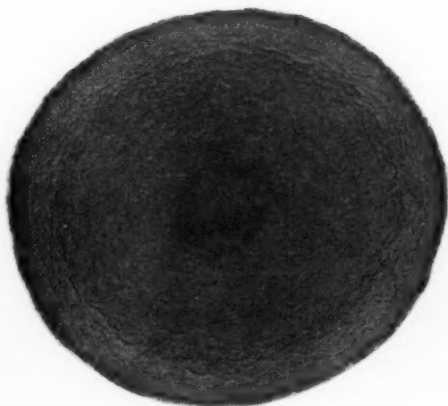
Pad–Jig

Pad–Jig

FIG. 2— Effect of Particle Size on Pad–Develop Processes

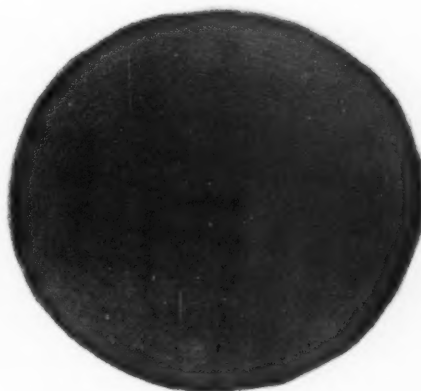FD Powder Fine   SQ Grains

Caledon Brilliant Purple 4R

Caledon Khaki 2G
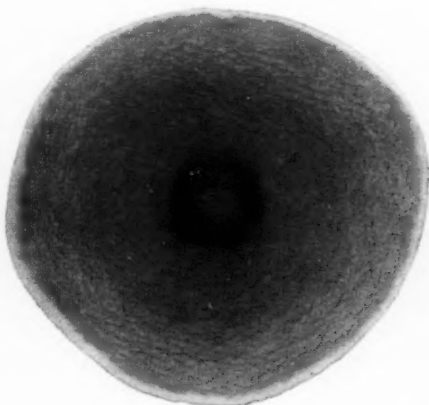
Caledon Dark Brown 6R

Fig. 3— Filter Paper Dispersion Tests illustrating Particle Size

1   Control

2   No addition

3   NaCl
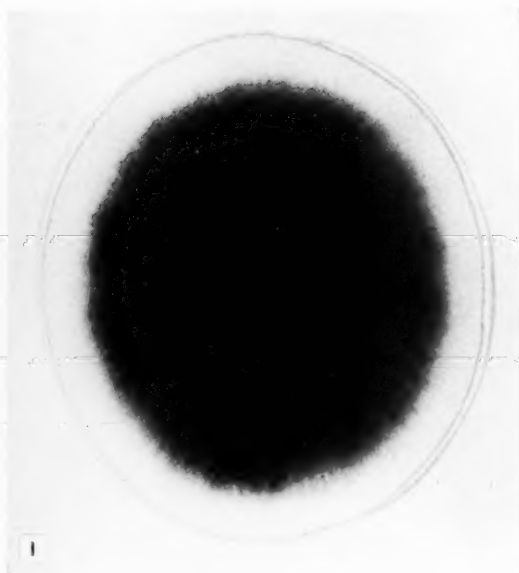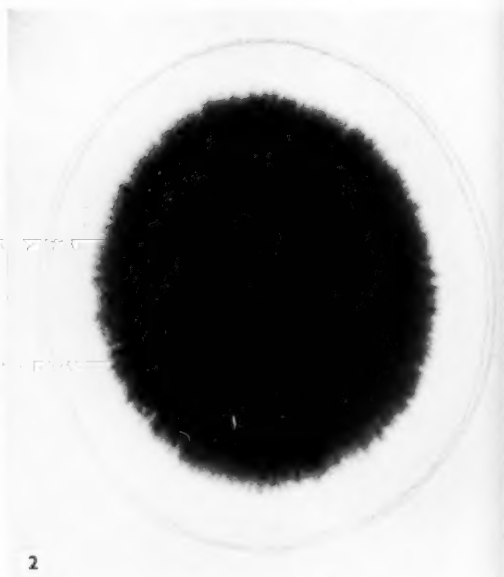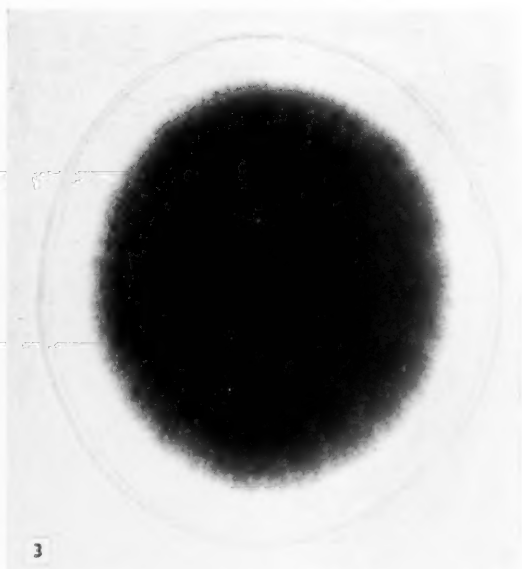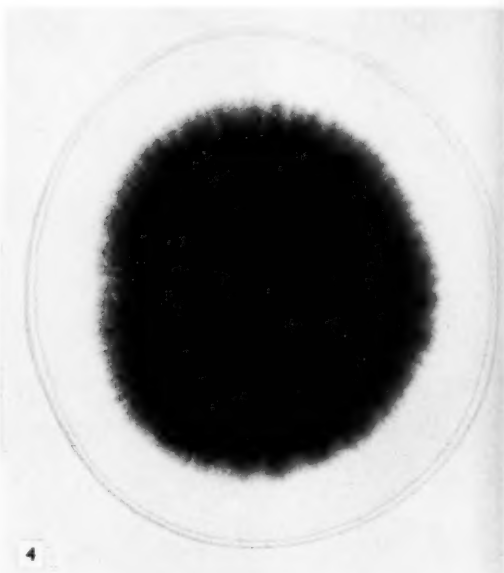
4   Na_2SO_4

FIG. 4— Effect of Additions to a Suspension of SQ Caledon Blue XRC Grains held at 80°c. for 1 hr.
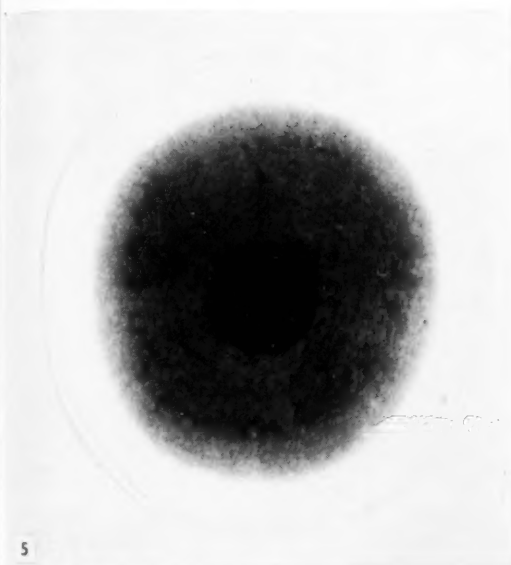
5

BaCl$_2$
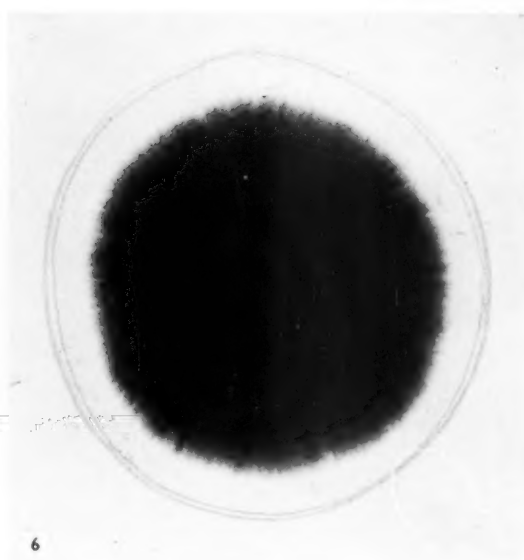
6

Suitable wetting agent
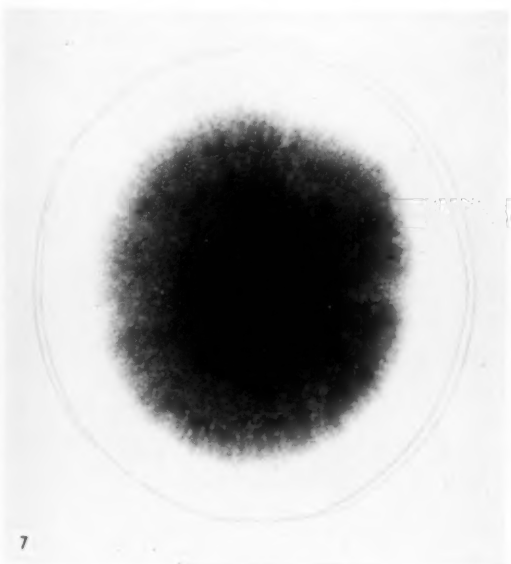
7

Suitable wetting agent + NaCl

8

Unsuitable wetting agent

Fig. 4—*continued*
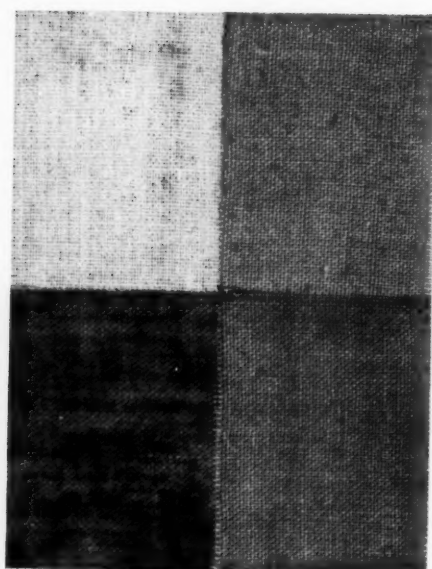
Caledon Brilliant Red 3B

Caledon Olive Green B
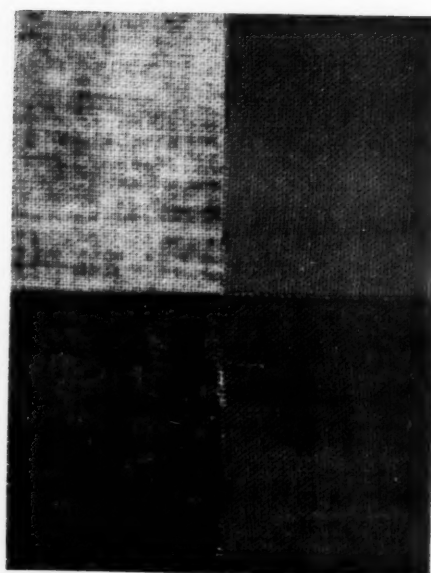
(a)   (b)   (a)   (b)

Caledon Khaki 2G
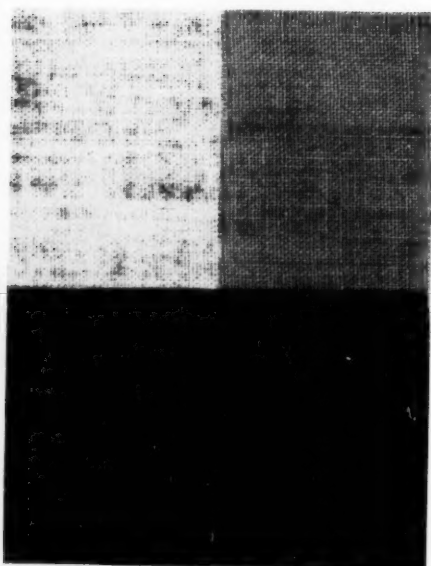
Caledon Dark Brown 6R
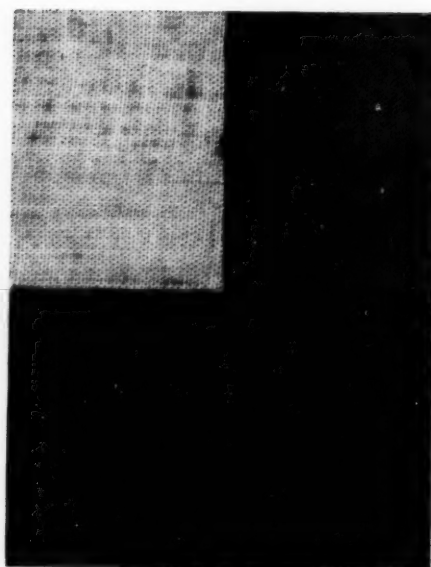
(a)   (b)   (a)   (b)

FIG. 5— Laboratory Test showing Effect of Migration Inhibitor V on Pigment Migration during Drying

TABLE I
Relation between Particle Size and Rate of Reduction

Dye	Particle Size Wt. % Material of Stokes Diameter—		Time of Reduction at 40°C. (sec.)	
	$<0.25\,\mu.$	$<3\,\mu.$	50% Reduction (t_{50})	95% Reduction (t_{95})
Caledon Gold Orange 3G	17·5	92·5	75	210
(C.I. 69025)	80·9	98·7	15	70
Caledon Brilliant Purple 4R	40·5	82·5	65	210
(C.I. 60010)	72·7	96·6	20	60
Caledon Dark Brown 6R	26·0	83·2	45	180
(C.I. Vat Brown 38)	73·2	97·1	25	80
Caledon Red BN	18·5	79·0	7	25
(C.I. 68000)	67·5	98·5	7	25

of a stable vat dye dispersion yielding satisfactory dyehouse performance is a complex physico-chemical problem.

The isolation of vat dyes during manufacture produces a highly flocculated mass of very coarse aggregates composed of primary particles. Each particle carries a negligible electric charge. The deflocculation of solid particles in aqueous media is achieved, for example, by paste milling with protective colloids, which may be low mol. wt., anionic polymers. During this process there is rapid formation of an electrokinetic charge and/or an hydrated sheath on the particles, which keeps them apart by repulsive forces and prevents reaggregation when the paste is converted to powder [6].

In addition to fine particle size, it is desirable that the dye should have the properties necessary for rapid reduction. Recent studies have shown that, with the majority of vat dyes, the finer the particle size, the faster will the dye be transformed from the insoluble keto to the soluble enol form in the presence of alkaline sodium hydrosulphite. In many cases, however, the dye will reduce rapidly, even in the coarse unmilled state.

Table I gives data for four anthraquinonoid vat dyes, each of which is represented by two samples showing appreciable differences in particle size distribution. In three cases a marked increase in fineness has produced a valuable increase in the rate of reduction, but the two samples of Caledon Red BN, although differing widely in particle size,

have identical t_{50} and t_{95} reduction times. Caledon Red BN is not alone in this respect, and other dyes displaying similar behaviour have been studied. Only in certain cases, therefore, is a fine particle size essential for obtaining rapid reduction. Experience in semi-scale trials has confirmed that vat dyes required for two-stage (pad–reduce) continuous application should reduce to the extent of 95% in less than 100 sec. at 40°C., as determined by laboratory measurements, if full tinctorial yield is to be achieved in bulk. This is particularly important when dyeing with the Standfast molten metal machine by the pigment pad–metal-bath reduction sequence, without intermediate drying, where speeds of 60 yd. per min. may be employed. Under such conditions a metal-contact time (effective reduction period) of only 3 sec. at ca. 95°C. is obtained, and dyes meeting the above specification will give optimum colour value.

Pigment paddings on cotton of fast- and slow-reducing samples of a series of dyes have been produced on the laboratory Standfast molten metal machine using metal-contact times of 3 sec. The differences in colour yields are illustrated in Fig. 1, whilst Table II gives the times of reduction and the corresponding relative colour values assessed by reflectance measurements and by optical measurements of extracted dye.

From Table II it is seen that, in general, a 10–25% increase in colour value was obtained with the faster reducing samples, but there is no direct relationship between the rate of reduction and

TABLE II
Relation between Rate of Reduction and Colour Value

Dye	Time of Reduction at 40°C. (sec.)		Relative Fixation (%)	
	50% Reduction	95% Reduction	By Reflectance*	By Extraction†
Caledon Gold Orange 3G	12	66	100	100
(C.I. 69025)	76	208	76	83
Caledon Brilliant Red 3B	20	39	100	100
(C.I. 67000)	48	256	88	90
Caledon Jade Green XBN	12	52	100	100
(C.I. 59825)	70	330	80	86

* Data obtained from spectrophotometric reflectance readings using the equation—

$$C = \frac{(1 - R)^2}{2R}$$

where $R = \%$ reflectance $\times 10^{-2}$ and $C =$ concentration.

† Samples were extracted with a mixture of sodium hydroxide, sodium hydrosulphite and Cellosolve.

percentage fixation for all vat dyes. The rate of reduction increases by a factor of 2·5–4·0 for a 20°c. rise [7], i.e. the increase varies from dye to dye. The increased fixation associated with rate of reduction is dependent on this temperature coefficient. A fine particle size is also required in order to minimise settling in aqueous suspension and to prevent visible speckiness on the padded fabric. It is particularly necessary to produce speck-free paddings for continuous reduction sequences, since insufficient time is available for redistribution and levelling, viz. 10–30 sec. in pad–steam processing and 3–7 sec. in the Standfast molten metal unit. Greater tolerance is permitted where pigment-padded goods are to be developed on the jig (40–60 min. reduction period), but levelling of even fine specks may not take place with dyes possessing a high strike and poor levelling properties.

A *coarse* suspension of Caledon Dark Blue 2R (C.I. Vat Blue 17), illustrated in Fig. 2 by a filter paper dispersion test, shows gross speckiness when pigment-padded on to mercerised poplin. It is seen from Fig. 2 that very little levelling has resulted from chemical padding and steaming; on the other hand, when the specky padding has been reduced for 45 min. in the jig, appreciable levelling has occurred, but many dye specks still remain. The *fine* suspension of the same dye is seen to yield speck-free dyeings, either with 30-sec. reduction in steam or 45-min. jig reduction.

The FD Caledon Powder Fine range, designed for pigmentation processes, has recently been strengthened and supplemented by a range of vat dyes described as *SQ Caledon Grains*. These dyes (in non-dusty grain form) have been specifically designed to possess the optimum particle size range consistent with first-class working properties in, for example, high-speed continuous dyeing sequences. This improved fineness over the FD Caledon Powders Fine is shown by the filter paper dispersion tests illustrated in Fig. 3; fineness is shown by increased colour intensity of the dispersion on the paper chromatogram and freedom from marked zoning with dispersion spread. In all cases this optimum fineness has resulted in the very fast reduction rate essential for continuous dyeing processes.

The very fine particle size produced in the manufacture of redispersible vat dyes must be maintained during their use in the dyehouse. The stability of fine pigment dispersions may be destroyed by high bath temperatures. They are similarly adversely affected if they are mixed with unsuitable padding assistants, electrolytes (particularly bi-, ter- and quadri-valent cations), strong acids or alkalis. Electrolytes in small amounts are frequently left in the goods after their preparation for dyeing. These may build up in the padding liquor to an appreciable concentration if a large trough is used. The water supply also may contain electrolytes, and if hard water is used some bivalent cations will be present. If two or more of the above factors operate simultaneously, particularly electrolyte plus wetting agent, complete flocculation of the dye can occur through repression of the repulsive forces operating between the primary dye particles. For continuous processing the dispersion should remain stable for several hours, and this is achieved by correct choice of padding assistant (if it is necessary to use one) and by limiting the storage temperature to a maximum of 50°c.

Fig. 4 illustrates the degree of flocculation of SQ Caledon Blue XRC Grains which occurred when various additions were made to an aqueous suspension held at 80°c. for 1 hr. The control suspension was prepared at 20°c. without addition and immediately spotted on to filter paper. The electrolytes employed were common salt, Glauber's salt, and barium chloride at concentrations of 20 g./litre. Uni-univalent (1:1) and uni-bivalent (1:2) electrolytes produced some aggregation, as shown by the lower colour intensity on filter paper. The addition of the Ba^{++} as barium chloride (2:1) caused severe aggregation and the intensity of the coloured area on filter paper was markedly reduced and larger aggregates were present at the centre. Of the two wetting agents used, one only caused some flocculation, and this effect is typical of padding assistants of the Calsolene Oil HS type. Such agents are satisfactory for use at 20–50°c., but at higher temperatures they cause some aggregation of the dye suspension. Effects similar to those produced by the 2:1 electrolyte will also occur if a wetting agent and an electrolyte are used together. Fig. 4 also shows the aggregation produced by a mixture of 5 g./litre Perminal PP and 20 g./litre common salt, although it is seen that the two, used separately, have little effect on the dispersion stability. The stability of the aqueous dye suspension itself was remarkably good under the conditions of test.

If flocculation of the type described is allowed to occur and settling proceeds to a serious extent, e.g. in the storage tank of a continuous padding range, it is not always possible to eliminate undesirable results on the cloth, even where a system of gentle agitation of liquor is used. A fine pigment sludge may form in the padding trough and fine pigment aggregates may adhere to the padding bowls. Speckiness, end-to-end tinctorial variations, and mark-off at sewings are examples of defects which can arise due to mishandling of vat dye dispersions.

INTERMEDIATE DRYING OF PIGMENT PADDED GOODS

In certain continuous dyeing sequences it is advantageous, and frequently necessary, to dry the pigmented fabric before reduction. Under adverse drying conditions there is a tendency for migration of the pigment to occur [8, 9]. This leads to colour unevenness in the finished goods, because of the absence of significant surface levelling during short reduction periods. Migration faults appear as back-and-face effects, side-to-centre effects, running direction streaks and fine or coarse blotchiness; the nature of the fault is determined to some extent by cloth geometry and the efficiency of the drier in respect of uniformity of temperature and hot air and steam movements. Laboratory drying techniques suitable for experimental work are seldom

completely comparable to those in use in bulk practice, and in order to assess the quality of dyeings obtained on the small scale it is often necessary to accentuate adverse conditions. In general, plant drying conditions (usually in hot-flue driers) may be adjusted to eliminate or minimise migration of dye. Unfortunately such experience is costly.

MIGRATION INHIBITORS

It is frequently possible to effect a marked improvement with regard to pigment migration faults by making suitable additions to the padding liquor, e.g. common salt, Glauber's salt, sodium bisulphite, sodium acetate and various types of common thickeners, but there are risks associated with this practice. Inorganic salts, for example, may lead to severe pigment aggregation (see Fig. 4) and poor penetration, even if the surface appearance of the dyeing is satisfactory. Some thickening agents, e.g. gum Tragacanth and sodium alginate, are difficult to prepare, and if not very carefully handled give fibrous residues on which pigment particles are adsorbed. Sodium alginate, however, when neutral and very carefully prepared in concentrations of up to 1 g./litre, is probably the most satisfactory.

Extensive laboratory investigations, which have yet to be confirmed by bulk trials, have shown that Migration Inhibitor V* (an organic polyelectrolyte of anionic character), when added to the pigment padding liquor, is very efficient in reducing these faults. This product is sold as a moderately viscous aqueous solution which is stable to hard water and completely and readily miscible with water, thus showing an advantage over thickeners of the alginate type. It has no adverse effect on the stability of pigment dispersions of FD Caledon Powders Fine and SQ Caledon Grains, even after 1 hr. at 80°c. Dyeings were produced on an open-weave cotton fabric by padding and drying under extremely severe conditions. Hot air at 90°c. from a commercial hair-drier was blown on to one side of the material, while the other side was exposed to the cool atmosphere. Evaporation of water was most rapid at the heated surface, so the dye migrated to this side. Such a test greatly accentuates migration, and the drying conditions are much more severe than would normally be found in bulk practice.

The effect of incorporating Migration Inhibitor V in suspensions of four vat dyes at the padding stage is clearly shown in Fig. 5. The patterns are mounted vertically in pairs to show the side on which the hot air impinged (the most intensely coloured pattern) and the side exposed to the

* Patents applied for

atmosphere (the least intensely coloured pattern). Paddings were dried (*a*) with no addition to the dye dispersion and (*b*) with the addition of 5 g. Migration Inhibitor V per litre. Concentrations of 2–10 g./litre in the padding liquor should be sufficient to eliminate migration, or reduce it to an acceptable level, under bulk conditions. The actual quantity required will be dependent on the drying conditions, the particular dye in use, the concentration of dye and the type of material being dyed. Migration Inhibitor V should be especially valuable where the sequence— pad, dry, chemical pad, steam— is in use.

This inhibitor makes a further valuable contribution to the efficiency of the dyeing process. The transfer of dye from pigment padded and dried material to solutions of sodium hydroxide and sodium hydrosulphite (generally referred to as "bleed") has been investigated. Two brands of two dyes were examined, viz. the SQ and FD brands of Caledon Brilliant Red 3B and Caledon Dark Brown 6R, using the pad–steam process, where the reducing liquor is padded on to the material before steaming. Various factors are operating simultaneously at this padding stage. Thus, some dye is transferred to the reducing liquor and begins to reduce, even at 20°c. Reduction of the dye on the fabric also commences. The dye which is building up in the trough and reducing is mechanically picked up and some surface dyeing will occur. Eventually an equilibrium is established. It was found that the addition of 5 g./litre Migration Inhibitor V to a padding liquor containing sufficient dye to give an 8·7% shade reduced the "bleed" of FD and SQ Caledon Brilliant Red 3B by a factor of 2 and that of FD and SQ Caledon Dark Brown 6R by a factor of 4.

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The Solubility of Wool Dyes

Its Assessment and Practical Significance

W. BEAL

Meetings of the West Riding Section held at the Victoria Hotel, Bradford, on 23rd October 1958, Mr. R. Heaton in the chair; and of the Midlands Section held at the College of Technology, Leicester, on 21st January 1959, Mr. A. W. Carpenter in the chair

The methods of testing the solubility of wool dyes at present in use are criticised and a new method is suggested. This method takes into account such variables as liquor : goods ratio, temperature at which dyeing is commenced, the dyeing assistants used, the type of water, the depth of shade being dyed, and the method by which the dyebath is prepared.

INTRODUCTION

Three main trends are discernible in the recent history of the dyeing industry.

First, dyeing machinery manufacturers have gradually developed more and more machines which pump dye liquor through the goods instead of circulating the goods through the liquor; for example, the Hussong machine has largely replaced the Klauder–Weldon.

A second major change has been the reduction in liquor : goods ratio used in dyeing. The old open pan, which was used for dyeing loose wool, etc., and in which the liquor ratio was as high as 50:1, was followed by machines such as the Psarski, Whitaker, and Calvert, in which the ratios were ca. 35:1. The modern loose wool or top dyeing machine employs a liquor ratio varying from 10:1 to 20:1. The reasons for this change are concerned with cost.

Almost all modern dyeing machines are made of stainless steel, which is very expensive, so the manufacturers aim at maximum capacity per unit weight of metal. Heating costs now form a major part of the total dyeing costs, and the lower the liquor : goods ratio, the lower the steam consumption. Since the exhaustion of dyes of almost all classes is inversely proportional to the liquor ratio, a low liquor ratio entails less wastage of dye.

In order to ensure levelness, a high rate of circulation of the dye liquor is required, and the pressure developed by the pump tends to compress the material and increases its filtering effect.

A third significant change is in the standard of fastness to wet processing. In many sections of the industry this is now much higher than it has ever been, and often necessitates the use of dyes of the highly aggregated milling or Polar type, since the brighter hues cannot always be obtained satisfactorily with chrome dyes or metal-complex dyes [1]. Milling acid dyes have much larger molecules than the level-dyeing acid dyes which

they are replacing, since it is a basic law in the synthesis of acid dyes that increased molecular size is needed to increase the wet fastness. Thus, the structure of Polar dyes is often similar to that of level-dyeing acid dyes, but an additional group is present, e.g. a toluene-*p*-sulphonyl chloride group; similarly, Carbolan dyes (ICI) have the structure of level-dyeing acid dyes, with an additional long alkyl chain. Examples illustrating this effect are (*a*) Erio Fast Blue SGR (C.I. Acid Blue 12) and Polar Navy Blue B (C.I. Acid Blue 94), and (*b*) Erio Fast Cyanine Green GS (C.I. Acid Green 25) and Carbolan Green G (C.I. Acid Green 27).

Increasing the molecular size has other effects besides increasing the wet fastness [2]. It increases the neutral-dyeing affinity of a dye. It also depresses the solubility in water, unless further modifications are made to the dye molecule.

THE PROBLEM OF INADEQUATE SOLUBILITY

One consequence of these three trends is that an ever-increasing number of dyeing faults can be attributed to the use of dyes of insufficient aqueous solubility. Many of the dyes now used are less soluble than those previously employed, whilst their concentration in the dyebath is higher, owing to the shorter liquor ratio. In circulating-liquor machines the material being dyed, e.g. cheeses or tops, acts as a filter for any dye which is not in solution.

Moreover, wool dyes are being used on many fibres other than wool or related animal fibres. Sometimes the conditions are similar to those used for wool, e.g. with Fibrolane (Courtaulds), but very often more acid has to be used to obtain exhaustion or penetration, and this acid may have an adverse effect on dye solubility [3]. With Acrilan (Chemstrand) more dye is required in order to produce a given depth (see Table I), thus increasing the concentration of dye in the bath.

In general, in order to produce the same depth on Acrilan as on wool, $1\frac{1}{2}$–3 times as much dye is

TABLE I

Shade No.	Wool : Acrilan Ratio		Wool		Acrilan
1	1 : 1·5	0·32%	Erio Fast Brown 5GL	0·48%	Erio Fast Brown 5GL
		0·2%	Erio Fast Rubine 3GS	0·3%	Erio Fast Rubine 3GS
		0·4%	Erio Anthracene Brilliant Blue 2GL	0·6%	Erio Anthracene Brilliant Blue 2GL
2	1 : 2	1·5%	Irgalan Grey BL	3·0%	Irgalan Grey BL
3	1 : 2·5	2·0%	Erio Fast Cyanine Green GS	5·0%	Erio Fast Cyanine Green GS
4	1 : 3	3·0%	Eriochrome Black PV 200%	9·0%	Eriochrome Black PV 200%

required when dyeing at 100°c. The discrepancy between the two recipes in Table I is greatest with full shades, i.e. just where solubility problems are likely to occur.

One obvious way to avoid these difficulties is to improve the aqueous solubility of dyes, but this may have an adverse effect on other properties. Thus, increased sulphonation results in a corresponding increase in skittery-dyeing properties and a decrease in covering power with a blend of different qualities of wool [4]; there is also a sharp decrease in neutral-dyeing and wet-fastness properties [5]. The solubility of a dye can be improved by various other means, e.g. by the use of certain auxiliary products, but this involves extra expense, so it is important to know when such an improvement is required.

SOLUBILITY TESTS

Most dye manufacturers quote figures for the solubility of their products, but these figures usually relate to the maximum concentration of dye which is soluble in a given volume of water at temperatures ranging from 90° to 100°c. This information is useful, but it does not enable the dyer to predict where trouble may arise, since most dyeings commence at lower temperatures, and usually in presence of acid and other dyeing assistants. Very often the solubility of the dye also depends on the electrolyte content of the water. Some dye manufacturers now indicate the sensitivity of their dyes to hard water, and, for special techniques such as padding, they give figures for the solubility of dyes at temperatures as low as 40°c.

What is required is a test which will provide solubility data that take into account—

(1) The amount of dye required to produce the shade

(2) The temperature at which dyeing is started

(3) The method by which the dyebath is prepared

(4) The hardness of the water or the softening process used

(5) The acid and other additions made to the dyebath.

NEW METHOD OF TEST

It is clearly not possible to give the solubility of every dye for all depths of shade, liquor : goods ratios, acid additions, etc. The method devised should be adaptable to any given set of conditions, so that each individual need can be satisfied, but some standard conditions must be accepted. The following conditions, which are as severe as any likely to be encountered in practice, were finally adopted.

Dye Solutions

Total volume of liquor	100 ml.
Liquor : goods ratio	12 : 1
(Implied weight of material)	8·5 g.

Percentage of dye and assistants (on weight of material)—

Blacks	9·0%
Blue-blacks and navy blues	6·0%
All other dyes	3·0%

Where dyes were found unsatisfactory under these conditions, further tests were carried out at one-third of the above depth.

pH Range

In order to cover a range of pH values, solutions were prepared with the following additions, all percentages being on the weight of material—

> No addition
> 1% Ammonia (0·880)
> 2% Ammonium sulphate
> 4% Acetic acid (40%)
> 4% Metachrome mordant

When required, solutions with the following additions were included—

> 2% Formic acid (85%)
> 4% Sulphuric acid (168°Tw.)

The acid additions are similar to those used in the Geigy wool graph system [6], but alkaline, neutral and formic acid conditions have now been included.

Temperature

Solubilities were determined at 40°, 60°, 80° and, where necessary, at 50° and 70°c. When testing chrome dyes by the metachrome method, however, care must be taken to allow for the fact that some combination between the dye and the chromate is likely to occur around 70–80°c.

Method of Test

(1) Dissolve the dye in 12·5 ml. water at b.p.

(2) Add 87·5 ml. water at such a temperature that the temperature after mixing drops to the desired figure

(3) Maintain the solution at this temperature for 10 min., adding the necessary assistants after the first 5 min. Keep the liquor well stirred

(4) Filter through a cloth (bleached unmercerised cotton, counts per in. 80/50s × 146/40s) preheated to the correct temperature.

This sequence of operations was chosen because it closely resembles the standard methods used on the works scale.

Assessment

The results obtained were assessed visually and given the following ratings—

> G = completely satisfactory
> F = satisfactory, but very slight precipitation
> P = unsatisfactory— moderate precipitation
> VP = unsatisfactory— heavy precipitation.

More exact methods of recording the amount of precipitation have been given [7], but it was desired to keep the system as simple as possible.

NOTES ON THE TEST

Bradford tap water was used for these tests; it has a low electrolyte content and 5° approx. hardness. With most dyes the solubility will not be appreciably different under these conditions from the results given in distilled water, but some dyes are extremely sensitive to hard water, e.g. Polar Red G (C.I. Acid Red 85). This dye is insoluble

A5

in Bradford water below 50°c. at normal concentration (3% on the weight of wool under neutral conditions), but in distilled water it is quite soluble at 40°c.

Although trouble is likely once the dye is precipitated in the bath, there are certain mitigating factors which should be recognised. The dye may be one which precipitates below a certain temperature and redissolves quickly above this temperature. If this is the case the migrating properties of the dye will also be very important, since they will decide whether any initial unevenness can be rectified. For this reason chrome dyes, when applied by the afterchrome method, are as a range much better than the fast-to-washing acid dyes, since the latter depend on their poor migration for their fastness to wet treatments.

Most of the migration ratings given in Table II were taken from the Geigy wool graphs and are based on the following scale—

Migration (%) from dyed pattern under specified conditions in 60 min.	Rating
<10	1
10–20	2
20–30	3
30–40	4
>40	5

Thus Eriochrome Red G (C.I. Mordant Red 17) has a migration rating of 5 when dyed by the afterchrome method with acetic acid, whilst Polar Red G has a rating of 2 when dyed with ammonium sulphate and 1 when dyed with acetic acid (see Fig. 1).

The ability of dyes to redissolve was determined by carrying out the normal test up to the filtration stage under conditions which would give precipitation, then reheating in 15 min. to 95°c. and filtering at this temperature. In most cases the first part of the test was carried out at 60°c., but where a dye was in solution at 60°c. and not at 40°c. the lower temperature was used. The results are given in Table II.

One problem was that of maintaining the selected temperature during filtration. A jacketed funnel is the obvious answer, but in order to save time an apparatus was constructed where four liquors could be filtered simultaneously while the temperature was maintained by a water jacket surrounding them all. Four-inch diameter funnels were used, and the filter cloths were of such a size that, when folded, the upper edge came to within 0·25 in. approx. of the rim of the funnel. Good reproducibility of results was obtained.

Tests were carried out in presence of the various assistants with which each dye may be applied, in order to determine which dyeing methods should be trouble-free, and the temperature was varied from 40° to 80°c. in 10° intervals. The liquor ratio chosen is about as low as is reached in practice, but it can be varied to suit individual requirements. Obviously, more trouble can be expected in package dyeing, where the liquor ratio may be as low as 12:1, than in a 40:1 ratio winch

Migration Curves
Upper curves— dye retained by dyed yarn
Lower curves— dye which has migrated to undyed yarn

– – – – –   0·9% Polar Red G conc., 2% ammonium sulphate and 10% Glauber's salt
· · · · · · · ·   0·9% Polar Red G conc., 5% acetic acid (30%) and 10% Glauber's salt
————   2% Eriochrome Red G, 5% acetic acid (30%) and 10% Glauber's salt
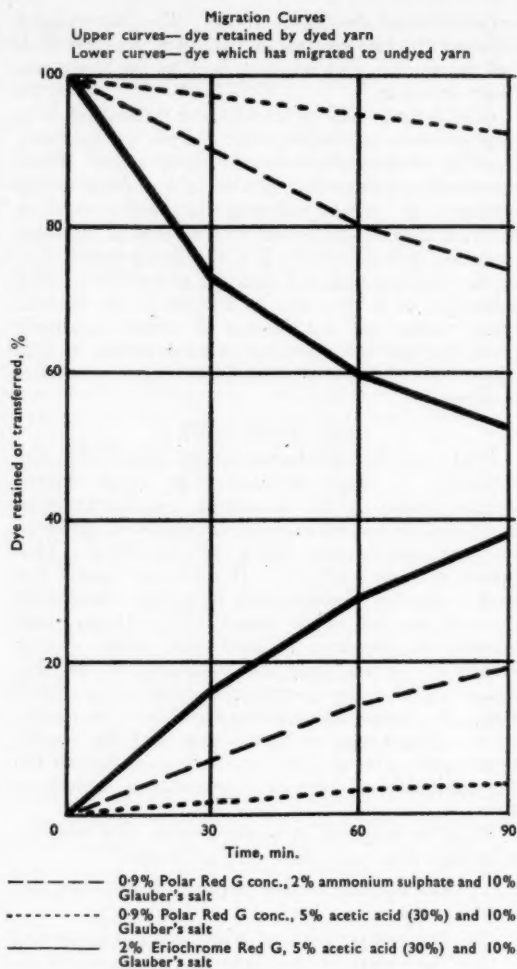
FIG. 1

dyeing. In the case of winch dyeing, the ratings in the columns of Table II headed "⅓ depth" correspond to the normal ratings for package dyeing.

Many fibres, especially wool and Acrilan, quickly absorb much of the acid added to the dyebath, thus tending to make the practical conditions less severe than those of the laboratory test, in which no material is used. This difference is accentuated if the material is pretreated in the acid liquor before adding the dye. Thus, if a dye is sensitive to acid (i.e. precipitated by acid), less trouble will occur in bulk than would be predicted on the basis of the test. Only rarely is a wool dye improved in solubility by increasing the acid content of the dye liquor, so the laboratory test will almost always be as severe as, or more severe than, the practical conditions.

Many dyes are absorbed quite rapidly by the fibre, so there will be less dye in solution as the temperature rises. This is important where the solubility of the dye varies inversely with the temperature.

TABLE II

Dye	Assistants	Solubility Ratings Temperature (°C.)						Reheated to—		Migration on 1-5 scale	Comments
		80°	70°	60°	50°	40°	60° in ½ depth	95°	95° in ½ depth		
Eriochrome Yellow SO (C.I. Mordant Yellow 3)	Ammonia	—	—	G	—	—	—	—	—	—	Satisfactory under all conditions tested.
	None	—	—	G	—	—	—	—	—	—	
	Metachrome mordant	—	—	G	—	G	—	—	—	—	
	Acetic acid	—	—	G	—	G	—	—	—	5	
Eriochrome Yellow G (C.I. Mordant Yellow 16)	Ammonia	—	—	G	—	—	—	—	—	—	Precipitated by acid. Satisfactory at and above 50°C. with metachrome mordant. Precipitates formed are very heavy and flocculent.
	None	—	—	G	—	—	—	—	—	—	
	Metachrome mordant	G	—	G	G	VP	—	—	—	—	
	Acetic acid	VP	—	VP	—	VP	F	VP	VP	5	
Eriochrome Red G (C.I. Mordant Red 17)	Ammonia	—	—	G	—	—	—	—	—	—	Satisfactory at all temperatures with metachrome mordant. Precipitated by acid. Precipitates are very light and fine.
	None	—	—	G	—	—	—	—	—	—	
	Metachrome mordant	G	—	G	—	G	—	—	—	—	
	Acetic acid	VP	—	VP	—	VP	P	P	F	5	
Eriochromal Red BG (C.I. Mordant Red 46)	Ammonia	—	—	G	—	—	—	—	—	—	Satisfactory neutral or alkaline. Precipitated by acid or metachrome mordant. Precipitates with metachrome mordant light and fine.
	None	—	—	G	—	—	—	—	—	—	
	Metachrome mordant	VP	—	VP	—	VP	VP	—	—	—	
	Acetic acid	VP	—	VP	—	VP	VP	VP	VP	3	
Eriochrome Black T (C.I. Mordant Black 11)	Ammonia	—	—	P	—	—	—	—	—	—	Satisfactory at and above 70°C.
	None	—	—	P	—	—	—	—	—	—	
	Acetic acid	G	F	VP	—	—	G	G	—	3	
Polar Scarlet GS	Ammonia	—	—	P	—	—	—	—	—	—	Satisfactory at all temperatures tested. Precipitated by alkali.
	None	—	—	G	—	—	—	—	—	—	
	Ammonium sulphate	G	—	G	—	F	—	—	—	2	
	Acetic acid	G	—	G	—	G	—	—	—	1	
Polar Red G conc. (C.I. Acid Red 85)	Ammonia	—	—	G	—	—	—	—	—	—	Satisfactory at and above 50°C. Unaffected by alkali.
	None	—	—	G	—	—	—	—	—	—	
	Ammonium sulphate	G	—	G	F	VP	—	G	—	2	
	Acetic acid	G	—	G	G	P	—	G	—	1	
Polar Red R conc. (C.I. Acid Red 99)	Ammonium sulphate	VP	—	F	G	G	G	VP	VP	1	Inversely soluble. Gelatinises above 60°C. with ammonium sulphate and above 50°C. with acetic acid.
	Acetic acid	VP	—	P	F	G	G	VP	VP	1	
Polar Brilliant Red BN conc. (C.I. Acid Red 130)	Ammonium sulphate	G	G	F	P	P	G	G	—	3	Satisfactory at and above 60°C. with ammonium sulphate. Gelatinises at and below 60°C. with acetic acid.
	Acetic acid	G	G	P	—	VP	G	F	G	2	
Eriochrome Brown R (C.I. Mordant Brown 33)	Acetic acid	G	—	G	—	G	—	—	—	5	Satisfactory, except when used with sulphuric acid.
	Formic acid	G	—	G	—	G	—	—	—	—	
	Sulphuric acid	VP	—	VP	—	VP	VP	—	VP	—	
Eriochrome Azurol B (C.I. Mordant Blue 1)	None	—	—	F	—	—	—	—	—	—	Not entirely satisfactory under any conditions. Precipitation much worse with sulphuric acid.
	Acetic acid	F	—	F	—	F	F	F	G	5	
	Formic acid	—	—	F	—	P	—	—	—	—	
	Sulphuric acid	—	—	VP	—	VP	VP	—	—	—	
Eriochrome Blue Black 2RCS (C.I. Mordant Black 17)	Acetic acid	F	F	P	—	VP	G	F	—	4	Solubility increases with strength of acid. Satisfactory at and above 70°C. with acetic acid, at and above 60°C. with formic acid, and at all temperatures with sulphuric acid.
	Formic acid	F	F	F	—	P	G	G	—	—	
	Sulphuric acid	G	—	G	—	F	—	—	—	—	
Acid Chrome Blue 2B (C.I. Acid Red 12)	Acetic acid	G	—	G	—	G	—	—	—	4	Satisfactory under all conditions tested.
	Formic acid	G	—	G	—	G	—	—	—	—	
	Sulphuric acid	G	—	G	—	G	—	—	—	3	

TEST CASES

It was decided that the only way to determine whether the test did in fact reproduce the conditions found in practice was to carry out the test with a selection of dyes whose behaviour under practical conditions was well known. Among the dyes used for this purpose (see Table II) were Eriochrome Yellow G (C.I. Mordant Yellow 16), Eriochrome Black T (C.I. Mordant Black 11), Polar Red G conc., and Polar Brilliant Red BN conc. (C.I. Acid Red 130).

The laboratory results obtained with various filter cloths and papers were then compared with practical results, and on this basis the filter cloths described above were chosen.

Eriochrome Yellow G is known to be unsuitable for use (above 1·0% approx. on the weight of wool) where the dye liquor circulates through a pack of material under acid conditions. Laboratory tests confirmed this fact, and showed that under neutral conditions the dye was satisfactory at and above 50°C.

Eriochrome Black T is usually applied with acetic acid. For many years it has been recommended that dyeing should start at or above 70°C.

in order to keep this dye in solution, and solubility tests have confirmed this recommendation.

Polar Red G conc. is sometimes stated to have poor levelness and rubbing-fastness. Solubility tests have shown that complaints about this dye can often be traced to the fact that dyeing commenced below 50°c.

Solutions of Polar Brilliant Red BN conc. are known to gel if the temperature falls too low. Solubility tests show that, although this gelling is more pronounced under acid conditions, either ammonium sulphate or acetic acid may be used as assistant, provided that dyeing is not commenced at too low a temperature. Laboratory tests also show that an assistant of the Irgasol PMC type greatly reduces this gelling.

Having established the method of testing, an attempt was made to correlate predictions based on laboratory tests with the results of practical trials.

(1) Two dyes were chosen, viz. Polar Red G conc. and Polar Red R conc. (C.I. Acid Red 99). Both dyes have given rise to rubbing faults, thought to be due to insufficient solubility. These dyes are usually applied with ammonium sulphate, but they can also be dyed with acetic acid. Tests showed that Polar Red G conc. was precipitated below 50°c., but was satisfactory above this temperature. Polar Red R conc., on the other hand, was insoluble at 80°c. but soluble at 40°c. Two single-cheese dyeings were carried out with each dye, one dyeing commencing at 40° and the other at 80°c. The results fully confirmed the results obtained in the tests. Polar Red G conc. gave a satisfactory result when dyeing was started at 80°c., but a poor result when dyeing was commenced at 40°c. With Polar Red R conc. the results were reversed.

(2) Laboratory tests show that Eriochrome Brown R (C.I. Mordant Brown 33) has very good solubility under all conditions, except when sulphuric acid is used (see Table II). In practice it can be applied satisfactorily on wool, using a mixture of acetic and formic acids, but it cannot be used for dyeing wool–Acrilan unions where sulphuric acid is required at the start, neither can it be used on shoddy which has been stripped with dichromate and sulphuric acid.

(3) Eriochrome Red G is a case where predictions are not borne out exactly in practice. No difficulties with regard to dye solubility would be expected when using the metachrome or the neutral method, but acetic acid precipitates some of the dye, though only in a finely-divided form. It would therefore appear that this dye should only be used in pale to medium depths with acetic acid in pack machines of low liquor ratio; but in fact it may be applied satisfactorily to cheeses, etc., in depths as high as 3·0%. The absence of trouble due to precipitation is explained either by the fact that only a little acid is used in the dyeing and that most of this is absorbed by the wool before the dye is added, or by the fact that the dye shows excellent migration.

(4) A dark peacock blue was required on Acrilan slubbing. A recipe based on Eriochrome Blue Black 2RCS (C.I. Mordant Black 17) and Eriochrome Azurol B (C.I. Mordant Blue 1) gave a dyeing in which dye was precipitated on the fibre, giving a bronzed effect of very poor fastness to rubbing. Laboratory tests confirmed poor solubility and indicated that the same shade dyed with Acid Chrome 2B (C.I. Acid Red 12) would be free from this fault. Bulk dyeings confirmed this prediction.

When Goodall [8] introduced his high-temperature dyeing method, he suggested that, if dyeing were commenced at 80–85°c., there would be much less danger of the dyes being out of solution than with a normal starting temperature of 40–50°c. However, in some cases, e.g. Polar Red R conc., the reverse applies and the dye shows inverse solubility. The most probable explanation is that, at high temperatures, such dyes hydrate and crystallise out. By means of the solubility test it is possible to predict quite accurately the temperature range over which the dye will certainly stay in solution, and to adjust the dyeing conditions accordingly. Of course, the usual factors which control levelness must not be ignored, and the temperature at which dyeing is commenced must be related to the pH, as well as to the rate of strike of the dye and its migrating properties. The Goodall high-temperature technique often needs less acid to exhaust a dye than does the normal method. The high-temperature method usually gives better rubbing-fastness in such cases, although it does not necessarily follow that a dye of poor solubility will give dyeings with poor rubbing-fastness, and vice versa. For example, Eriochrome Black A (C.I. Mordant Black 1) has poor solubility under acid conditions, but gives dyeings of very good rubbing-fastness. Conversely, Polar Red 3B (C.I. Acid Red 134) has good solubility, but gives dyeings of comparatively poor rubbing-fastness. It has often been found that, when complaints of poor rubbing-fastness occur, the dyer has had to employ an unusually large amount of acid to exhaust the dyebath, owing to the fact that the dye was not completely in solution at the start of dyeing. When conditions have been modified, both troubles have disappeared. In many cases the colour yield obtained from a given recipe is greatly increased when the dye is kept in solution throughout the dyeing, as compared with a faulty method of application. In the former case the dye is more likely to be evenly distributed throughout the material, whereas in the latter case dye aggregates are deposited on the fibre without giving a complete coverage. A parallel is given by comparing a dyeing on slubbing of a dye in, for example, 3% depth with a blend made by mixing equal quantities of a 6% dyeing and undyed material. The latter appears only about half as deep, although it contains the same amount of dye.

USE OF AUXILIARY PRODUCTS

The solubility of a dye can often be greatly improved by adding an auxiliary product to the dyebath. Polar Brilliant Red BN conc. has already been mentioned in this connection; another example is Eriochromal Red BG (C.I. Mordant Red 46). This latter dye gives better exhaustion than the better-known Eriochrome Red G under metachrome conditions, but in practice it could only

be used for pale to medium depths in package-dyeing. As predicted, an addition of Irgasol PMC to the dyebath increases the solubility of this dye and enables it to be used for virtually any depth.

The addition of an auxiliary product, however, does not necessarily improve the solubility of a dye. Many of the new dyeing techniques depend on the use of a compound, one effect of which is to reduce the solubility of the dye in the bath. These "marginal" techniques, where the solubility of the dye in the bath is reduced to a minimum, are usually used with synthetic fibres or mixtures containing them. They depend on the formation of a loose complex of the dye with the auxiliary product, thus preventing a rapid strike. A typical example is in wool–Acrilan dyeing, where a high concentration of sulphuric acid is often present at the start [9, 10]. Such conditions are unsuitable for milling acid dyes and some chrome dyes, and a dyeing assistant has to be added in order to lower the rate of strike and so prevent uneven dyeing. Non-ionic dyeing assistants have insufficient restraining action, whilst anionic compounds adversely affect the solidity of shade. Mildly cationic assistants give an acceptable rate of strike and a solid shade, but are liable to cause some precipitation with anionic dyes. By using the laboratory test, modified to suit the actual conditions, the tendency to precipitate can be illustrated and a way found to overcome this difficulty. Practical dyeings confirmed that the fault disclosed by the test was real and very troublesome, but the remedy suggested prevented this fault in subsequent dyeings.

A comparable case occurs when dyeing acrylic fibres with basic dyes by the Geigy IT method [11]. It had previously been found that basic dyes of the Maxilon type had a marked critical temperature around 90°c. when applied to acrylic fibres of the Orlon (DuP) and Courtelle (Courtaulds) type. Cationic and non-ionic assistants did not give sufficient restraining effect, but anionic assistants showed a marked restraining effect without unduly affecting the final exhaustion. Tests showed, however, that most anionic textile chemicals precipitate basic dyes under normal dyebath conditions, but certain anionic compounds, e.g. Irgasol DA, are much better than others. When, in addition, a non-ionic compound was added as an anti-precipitant, the mixture gave adequate restraining action without precipitation, and has proved satisfactory in practice.

CONCLUSIONS

Many of the test results have been compared with those obtained in practical trials. In many cases these trials substantiated the laboratory tests, but with Eriochrome Red G, as already mentioned, practical trials gave no indication of trouble due to inferior solubility, when it might have been expected. This discrepancy may be due to the use of filter cloths which were too fine, or to any of the other reasons given. On the other hand, there have been isolated cases where the reverse applied. It is obvious that the laboratory test does not reproduce practical conditions exactly, owing to the absence of the fibre, but it is believed that it represents an important advance over previous test methods.

It is hoped that the information given by this type of solubility test, together with information on dyeing properties of the type supplied by the Geigy wool graph system, will enable the dyer to predict where faults are likely to occur and so avoid them by choosing a satisfactory dyeing method. This method of testing the solubility of dyes under dyebath conditions should also help to eliminate differences between laboratory results and works practice, and thus be of real assistance to the dyer.

*   *   *

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COMMUNICATION

The Migration of Non-substantive Dyes on Fabrics and its Relation to Saturation Regain and Fibre Surface Structure

D. WILSON

The migration of non-substantive dyes on fabrics woven from a range of fibres has been studied at room temperature and the regains below which migration does not occur, i.e. the critical regains, determined. It has been found that for most fibres the critical regain is just below the imbibition value and is independent of the dye used to determine it. However, this is not so for viscose rayon, where the critical regain depends on the molecular size of the dye. This effect is caused by the presence of small continuous channels in the surface of viscose rayon fibres, which are flooded and can therefore transport dye at humidities less than saturation. The use of a non-penetrative dye-restrainer complex in determining the amount of surface water left on fibres after centrifuging is described, and the results combined with the critical regain determinations to clarify the behaviour of fibre–water systems at high humidities and to estimate "true" saturation regains.

1. Introduction

For many years it was generally believed that the absorption saturation regain of viscose rayon was about 40%[1]. In contrast to this, the imbibition value determined by the standard procedure (centrifuged for 5 min. at 1000 g), which is taken to give the desorption saturation regain, was about 80–100%. The hysteresis loop therefore appeared to be open at saturation, this being true for other fibres also[2-9]. Thermodynamically, however, there should be no difference between immersion in water and in a saturated atmosphere, so this apparent difference between the absorption and desorption values was difficult to understand. Ashpole[10], however, made fresh determinations of absorption isotherms at very high humidities (i.e. 98% R.H. and above) using a more refined experimental technique than those used in the earlier investigations. He found that the adsorption saturation regain and the imbibition value corresponded very closely to each other, thus showing that the hysteresis loop did in fact close at 100% R.H.

The results of many indirect methods of determination still pointed, however, to a value of 40% for the saturation regain of viscose rayon, any moisture in excess of this being assumed to be in the form of "free" or "liquid" water[11-19]. In particular the migration experiments of Preston and Bennett[16] apparently gave a direct indication of free water being present down to a regain of 40%.

This paper is concerned with an extension of these experiments, and an interpretation of the results is put forward which resolves the former discrepancies.

2. Experimental

2.1 PRINCIPLE OF THE EXPERIMENTS

If a piece of wet fabric is laid out on a glass plate with part of its upper surface covered, e.g. by a microscope slide, little or no evaporation of moisture will take place from the covered area compared with that from the uncovered. As the uncovered area dries, therefore, there will be a moisture-concentration gradient from the covered to the uncovered areas. This will cause the moisture to move from the covered to the uncovered areas in the following ways—

(1) By diffusion through the bulk of the material

(2) By movement of "liquid water" along small channels in the surface of the fibres, or between fibres.

The second mechanism can be operative only as long as there is "surface water", which may be defined as water outside the geometrical outline of the fibres, present in channels on the material; movement of moisture by this means will therefore not take place if the regain of the sample, when drying commences, is such that no surface water is present. A very simple way of detecting such movement of surface water is to use a non-substantive dye as a tracer. By observing the drying of a series of samples with different known initial regains, it should be possible to determine the regain at which surface water ceases to be present, this being known as the *critical regain*. Using this principle with Azo Geranine 2GS as a tracer, Preston and Bennett[16] obtained the value of 40% regain for viscose rayon and identified this with the saturation regain.

2.2 EXPERIMENTAL METHOD

The experimental method used is very similar to that used by Preston and Bennett. Samples of fabric are soaked in the appropriate dye solution at room temperature, surplus solution is blotted off, and the samples dried in air at room temperature to different regains. These regains are found by initially weighing the samples when in equilibrium with an atmosphere at 65% R.H., determining their regain in this condition by oven-drying other identical samples, and thus calculating a dry weight for each sample. This known, the regains during drying are calculated in the usual way from the sample weights.

When the samples have been brought to the required regains, they are laid out on glass plates with part of their upper surface covered by a microscope slide under a load of about 50 g. and left to dry overnight at 65% R.H. and 70°F. The samples are then inspected, in order to discover whether any migration has taken place.

This technique, using a range of dyes as tracers, has been applied to fabrics woven from the following yarns—

Continuous filament: viscose rayon, Dicel and M95*
Spun yarns: Fibro, M95, Toramomen*, wool and cotton.

* M95 and Toramomen are modified viscose fibres.

Other fabrics used were made from Fibro yarns and had been either (*a*) steamed or (*b*) cross-linked by formaldehyde to reduce the imbibition. Constructional details of these fabrics are given in the Appendix.

The range of dyes used includes, in particular, some direct dyes to which either Albigen A (BASF) or Tinegal W (Gy) had been added; these restraining agents, when present in sufficient quantity, prevent the penetration of certain dyes into the fibres [20]. This enables the amount of surface water remaining on samples after centrifuging to be determined directly in the following way—

A sample is soaked in a relatively large volume of the solution containing the dye–restrainer complex, removed, and centrifuged. This leaves a slight trace of colour on the sample which must be contained in the surface water, and which is washed off in a known volume of water and estimated colorimetrically. Assuming that the concentration of dye in the surface water left on the sample after centrifuging is the same as that of the original bulk solution, and that there is no adsorption of the complex on the fibre surface, the volume of surface water remaining on the sample after centrifuging may be calculated. If there is any slight adsorption of the complex on the fibre surface, the values found for surface water will be greater than the true values and may therefore be regarded as maximum values.

3. Results

3.1 CRITICAL REGAINS

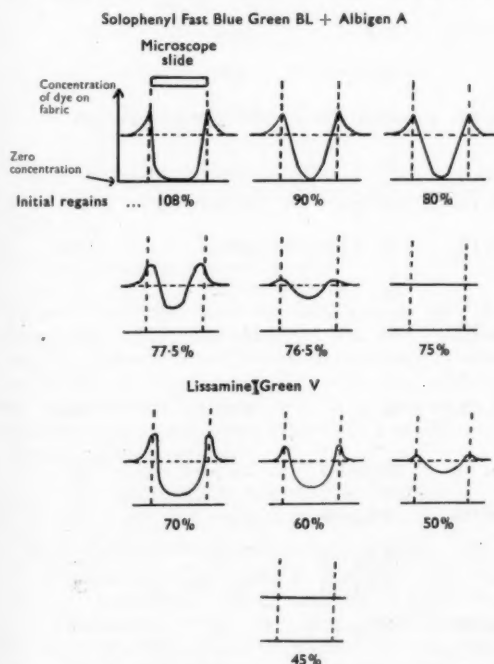The values found for critical regain, imbibition, and surface water remaining after centrifuging are given in Table I. In the column giving results of surface water determinations, blanks occur when acid dyes were used, as these penetrate the fibres and thus make the estimation of surface water by their means impossible. The form of migration which was observed is illustrated diagrammatically in Fig. 1.

There are two main points to note in these results—

(1) In all cases where a non-penetrative complex was used, and surface water remaining after centrifuging was measured, the following relationship is found—

$$\text{Critical Regain} + \frac{\text{Surface Water remaining after Centrifuging}}{} = \frac{\text{Imbibition Value}}{}$$

(2) The critical regain for normal viscose rayon (in both the continuous-filament and staple forms) and for steamed viscose rayon covers a considerable range, the value obtained depending on the dye used to determine it. For all other fibres the critical regain found is virtually independent of the dye used.

3.2 MIGRATION ON VISCOSE SHEET

In order to determine whether the dye was capable of moving through the body of the fibres to any appreciable extent, a similar migration experiment was carried out with Azo Geranine 2G on viscose sheet. No migration occurred below the imbibition value, so it was concluded that diffusion of dye through the body of the fibres does not contribute significantly to the observed dye migration in woven fabrics.

3.3 RATE OF DRYING

The drying of Fibro and M95 staple fabrics under the conditions of the experiment was followed as a function of time from regains just below the critical regains given by the Albigen A complex. The results are illustrated in Fig. 2.

3.4 FIBRE CROSS-SECTIONS

Cross-sections of the cellulosic fibres are illustrated in Fig. 3. M95 and Toramomen have smooth cross-sections, in contrast to the deeply indented
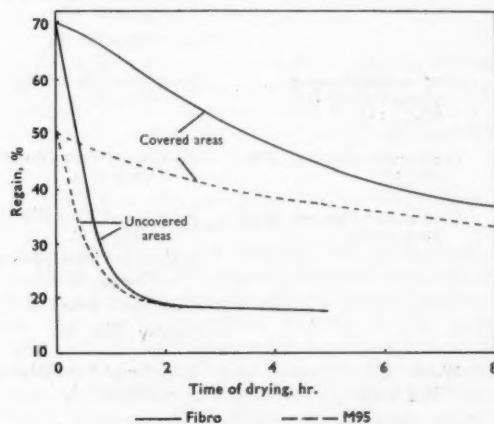

FIG. 1— Diagrammatic Representation of Migration on a Fabric made from Fibro Yarns

FIG. 2— Drying Curves for Fibro and M95 Staple Fabrics

TABLE I

Fabric and Imbibition	Dye Solution	Critical Regain (%)	Surface Water (%)	Total (%)
	Non-penetrative Restrained Dyes			
Fibro (I) 83±1%	Solophenyl Fast Blue Green BL +Albigen A	76 ±1	8·5±0·5	84·5
	Chlorantine Fast Blue 3GLL +Albigen A	75 ±1	9·5±0·5	84·5
	Solophenyl Fast Blue Green BL +Tinegal W	70·5±1	13 ±1	83·5
	Durazol Blue 2GN +Tinegal W	71 ±1	11 ±1	82
	Penetrative Acid Dyes			
	Carbolan Blue B	65 ±1	—	—
	Coomassie Blue RL	60 ±1	—	—
	Azo Geranine 2G	52 ±2	—	—
	Solway Blue BN	50·5±1	—	—
	Lissamine Green V	45·5±1	—	—
Fibro (II) 80±1%	Solophenyl Fast Blue Green BL +Albigen A	70 ±1	11 ±1	81
	Lissamine Green V	42 ±1	—	—
Steamed Fibro 61±1%	Solophenyl Fast Blue Green BL +Albigen A	50 ±1·5	12 ±1	62
	Lissamine Green V	41 ±1·5	—	—
Cross-linked Fibro 36·5±1·5%	Solophenyl Fast Blue Green BL +Albigen A	30·5±1·5	8 ±1	38·5
	Lissamine Green V	30 ±1·5	*8 ±1	38
M95 staple 64±1%	Solophenyl Fast Blue Green BL +Albigen A	53 ±1	8 ±1	61
	Coomassie Blue RL	54 ±2	—	—
	Azo Geranine 2G	50 ±2	—	—
	Lissamine Green V	50 ±2	—	—
Toramomen staple 50±1%	Solophenyl Fast Blue Green BL +Albigen A	45·5±1	—	—
	Lissamine Green V	45 ±1	—	—
Cotton 46·5±2%	Solophenyl Fast Blue Green BL +Albigen A	32 ±1	12 ±1	44
	Lissamine Green V	31 ±1	—	—
Continuous-filament viscose rayon (I) 98±3%	Solophenyl Fast Blue Green BL +Albigen A	82 ±2	12 ±1	94
	Solophenyl Fast Blue Green BL +Tinegal W	85 ±2	10·5±1	95·5
	Azo Geranine 2G	60 ±2	—	—
Continuous-filament viscose rayon (II) 97·5±1%	Solophenyl Fast Blue Green BL +Albigen A	83 ±1	15 ±1	98
Continuous-filament M95 70±1%	Solophenyl Fast Blue Green BL +Albigen A	61 ±1	9·5±1	70·5
Continuous-filament Dicel 23·5±0·5%	Solophenyl Fast Blue Green BL +Albigen A	19·5±0·5	3·5±0·5	23
	Solophenyl Fast Blue Green BL +Tinegal W	19·5±0·5	—	—
	Coomassie Black B	19·5±0·5	—	—
	Solway Blue B	19·5±0·5	3·5±0·5	23
Wool 50±1·5%	Solophenyl Fast Blue Green BL +Albigen A	46 ±1	—	—

* It was found that Lissamine Green V did not penetrate cross-linked Fibro.

section of normal viscose rayon, as well as possessing a lower imbibition. When examined in the dry state under a normal optical microscope, steamed and cross-linked viscose rayon were found to have cross-sections identical with those of normal viscose rayon. It is possible, however, that differences could be detected by electron-microscope studies.
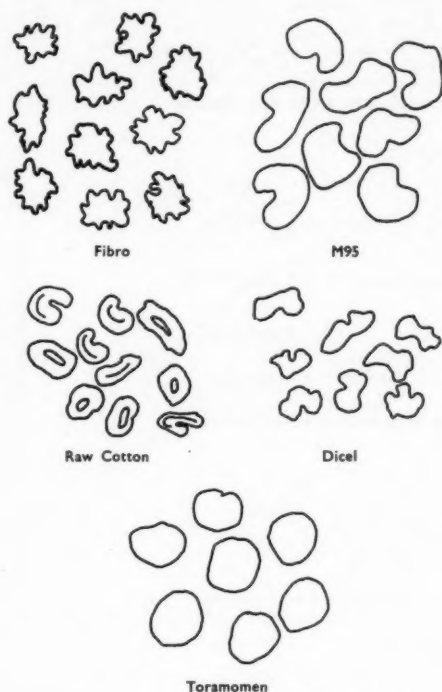

FIG. 3— Cross-sections of Dry Cellulosic Fibres

4. Interpretation of the Results

4.1 INTRODUCTION

The discussion is based on the two points noted in § 3.1. The relationship found for non-penetrative dyes, viz.—

Critical Regain + Surface Water remaining after Centrifuging = Imbibition Value

shows that the moisture containing the dye remaining after centrifuging, i.e. the "surface water", is the same as that which permits migration of the dye during drying. Before dealing with the second observation, however, it is necessary to clarify some points with regard to the cellulose–water system in general.

4.2 THE CELLULOSE–WATER SYSTEM

4.2.1 *Initial Assumptions*

Two initial assumptions must be made, viz.—

(1) That the R.H.–regain isotherm for high humidities determined by Ashpole [10] is correct (Fig. 4) and that previous determinations at these high humidities were incorrect owing to inadequate experimental techniques.

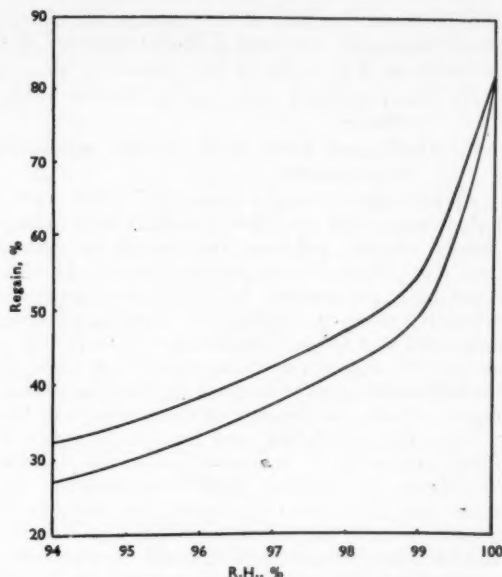FIG. 4— The Hysteresis Loop for Viscose Rayon close to Saturation

(2) That the relationship between the vapour pressure over a cylindrical liquid surface and the curvature of the surface is given by an equation similar to the Kelvin equation for spherical surfaces [21] and that the equation is valid down to quite small radii of curvature (say about 200A).

The equation is—

$$\ln\left(\frac{p_0}{p}\right) = \ln\left(\frac{100}{\%\,\text{R.H.}}\right) = \frac{M\gamma}{RT\varrho r}$$

where—

p_0 = saturated vapour pressure of the liquid at temperature T

p = actual vapour pressure over the curved surface at temperature T

ϱ = density of the liquid (taken to be 1·0 for water)

M = mol. wt. of the vapour (taken to be 18 for water vapour)

γ = surface tension of the liquid (taken to be 72 dynes/cm. for water)

r = radius of the cylindrical surface

T = absolute temperature

R = gas constant

The value of $\ln(p_0/p)$ is half as large as it would be for the same value of r in the Kelvin equation because the surface has only one direction of curvature, in contrast to a spherical surface which has two.

4.2.2 *Equilibrium of Imbibed and Capillary Condensed Water*

In partially swollen cellulose, the water absorbed in the cellulose is in equilibrium with a particular relative humidity, the exact equilibrium depending on the previous sorption history of the sample (absorption–desorption regain hysteresis). Ashpole's work [10] has shown the great sensitivity of regain to relative humidity at R.H. values greater than about 96%, when small capillaries or channels must be flooded. If, therefore, the cellulose contains

capillaries or channels of the appropriate dimensions, the regain measured at high humidities will be made up of moisture in two states—

(1) Truly imbibed water, in the interior of the cellulose

(2) Condensed water, held in small capillaries and channels.

At first sight it might seem that water in the liquid state could not exist in contact with incompletely swollen cellulose, but would be sucked into the cellulose by absorption forces. At high humidities and regains, however, the absorption forces for water in cellulose are very small, even compared with those operative at 65% R.H. [22] (i.e. about 15% regain for viscose rayon). A curve of the differential heat of sorption for water in viscose rayon, which is a measure of the strength of the water–cellulose bonding, as a function of regain is illustrated in Fig. 5. It is seen that, in the range of humidities and regains under consideration, i.e. above 96% R.H. or 40% regain, the strength of bonding is extremely close to that in liquid water. In addition, the water held in small capillaries has a reduced activity compared with normal liquid water, the activity being given by the relative vapour pressure, p/p_0, which can be calculated from the equation given in §4.2.1. Since at any particular regain the imbibed water and the capillary condensed water are in equilibrium with the same relative humidity, they must also be in equilibrium with each other.

4.3 THE EFFECT OF THE MOLECULAR SIZE OF THE DYE ON THE CRITICAL REGAIN

It has been noted previously (§3.1) that the critical regain for normal viscose rayon and Fibro
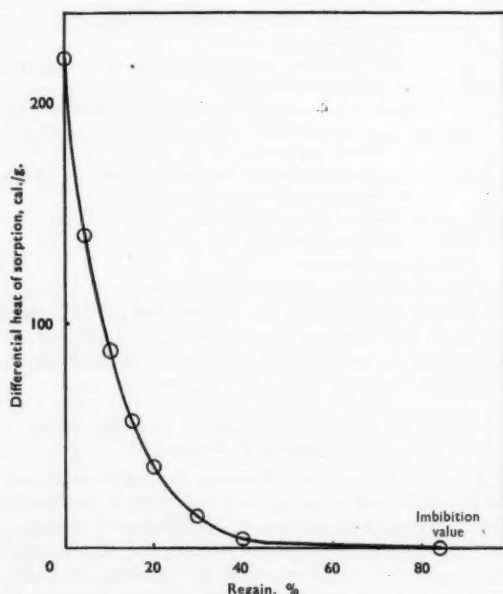
This curve was obtained by extrapolation of results by the Ashpole-Cooper method[22]

FIG. 5— Differential Heat of Sorption vs. Regain of Viscose Rayon

is dependent on the dye used to determine it. The formulae and approximate value of the largest dimension D of the dye molecules used are as follows. Bond lengths used in calculating the dimensions were taken from values given by Evans [23].

D

30 A.

Carbolan Blue B (C.I. Acid Blue 138)

17 A.

Coomassie Blue RL (C.I. Acid Blue 92)

14 A.

Azo Geranine 2G (C.I. Acid Red 1)

13 A.

Solway Blue BN (C.I. Acid Blue 45)

11 A.

Lissamine Green V (C.I. Acid Green 16)

$n = 30$ approx.

Large but indeterminate. Probably at least 50 A.

Albigen A
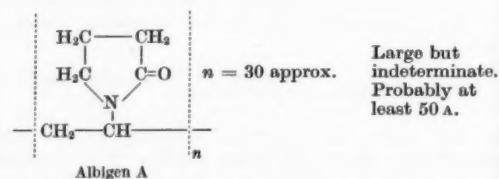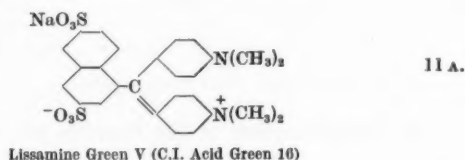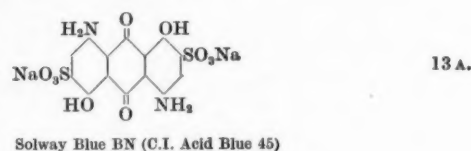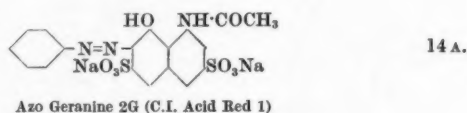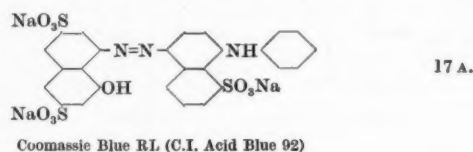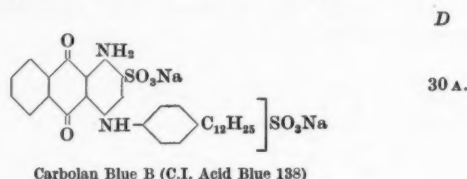
If it is assumed that channels do exist in the surface of normal viscose rayon and Fibro, the half-width r of the largest channel flooded at any given regain can be found by means of the isotherm determined experimentally by Ashpole and the equation given in §4.2.1. The results of this calculation for desorption are given in Table II, and a plot of $1/D$ against $1/r$ is illustrated in Fig. 6. There appears to be a distinct correlation between the size of the dye molecule and the width of the largest channel flooded when migration of that particular dye ceases. This suggests that the range of critical regain found for Fibro may be due to the presence of surface channels of the sizes calculated.

TABLE II

Critical Regain (%)	R.H. (%)	Half-width of Largest Channel Flooded, r (A.)	Size of the Dye Molecule, D (A.)	$1/r$ (A.$^{-1}$ × 10^{-3})	$1/D$ (A.$^{-1}$ × 10^{-3})
75	99·75	2130	—	0·47	—
71	99·62	1400	—	0·71	—
65	99·44	950	30	1·05	33
60	99·44	700	17	1·43	59
52	98·74	440	14	2·27	71
50·5	98·54	360	13	2·78	77
45·5	97·70	230	11	4·35	91

FIG. 6—$\frac{1}{D}$ vs. $\frac{1}{r}$

FIG. 7
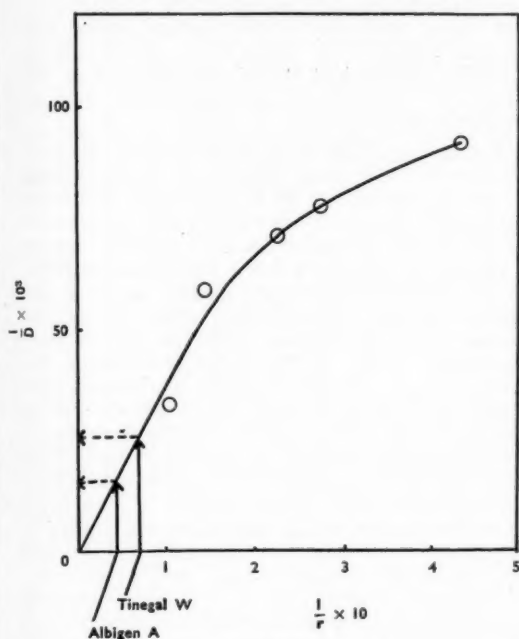
4.4 CROSS-SECTIONS OF FIBRES AND POSITION OF THE CHANNELS

Typical cross-sections of viscose rayon, M95, Toramomen, cotton and Dicel fibres are illustrated in Fig. 3. That of viscose rayon is the only one which is not smooth in outline. The channels postulated for viscose rayon are too small to be resolved by normal light microscopy, where the limit of resolution for practical purposes is about 5,000 A., but support for their existence is given by electron microscope photographs [24], [25], [26], where channels may be seen in the indentations between the lobes of the fibre.

4.5 ANALYSIS OF THE MIGRATION EXPERIMENT

The simple migration experiment will next be analysed. The R.H. distribution across the fabric will be of the form illustrated in Fig. 7.

The magnitude of the R.H. step under the microscope slide will be zero when the fabric is first laid down, but will rapidly become significant as the uncovered areas dry more quickly than the covered. The system when the R.H. step is appreciable may therefore be considered.
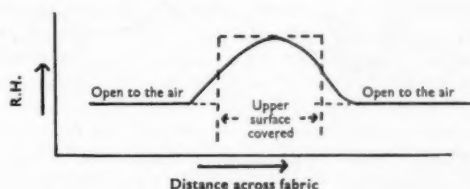
As long as the regain of the covered area is greater than the saturation regain, surplus "surface water" is present and the equilibrium humidity will remain at 100% R.H. As this surface water drains away under the action of surface tension forces, transporting dye in the process, the equilibrium R.H. remains at 100% and all channels and pores remain filled until the regain drops below the saturation value. When this stage is reached the surface of the liquid in small channels takes up a curvature given by the equation in § 4.2.1, and, assuming zero contact angle, will be tangential to the sides of the channel (Fig. 8).
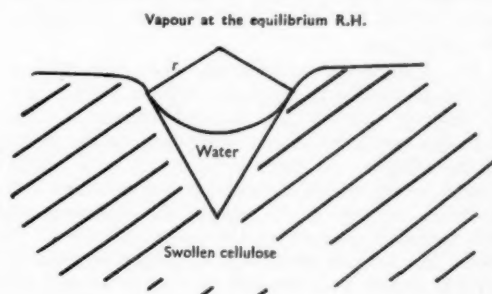
FIG. 8

The depth of liquid in a channel of V-shaped cross-section will therefore depend on the curvature of the liquid surface, and hence on the R.H. and the regain of the cellulose. If it is now imagined that more water drains from the channel, the level in the channel will fall, thereby reducing the radius of curvature of the surface and the equilibrium R.H. The equilibrium between the water in the channel and the prevailing R.H. may be restored in two ways—

(1) By increasing the volume of water in the channel, thereby increasing the radius of curvature of the liquid surface

(2) By decreasing the prevailing R.H.

The volume of water in the channel may in turn be increased in two ways (Fig. 9)—

(1) By water diffusing directly from the swollen cellulose into the channel, transporting dye with it

(2) By water vapour condensing in the channel, having evaporated from the swollen cellulose; this in turn also has the effect of reducing the R.H. above the channel.

(1)   (2)
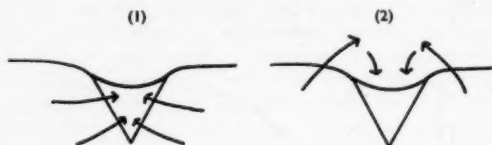
FIG. 9

These two mechanisms probably occur simultaneously. The overall effect will be that the regain of the cellulose, the equilibrium R.H. and the level of water in the channels fall; all three, however, remain in equilibrium with one another.

There are two possible mechanisms by which the transport of dye along flooded channels may be stopped, viz.—

(1) A spatial mechanism, when the channels remaining flooded are so small that the dye molecules can no longer move along them. This leads directly to a particular R.H. below which transport of dye must cease, which in turn means that there is a particular regain— the critical regain— below which migration of the dye cannot take place. If, as seems likely, the critical size of channel depends on the molecular size of the dye, then so also will the critical regain. This is the effect which has been found for Fibro and continuous-filament viscose rayon.

(2) A diffusion mechanism, when the diffusion of dye molecules through the cellulose is too slow to supply dye to the flooded channels. This diffusion rate is markedly dependent on the regain of the cellulose, so there is likely to be a critical regain below which it becomes insignificant. In addition, at any given regain, the diffusion rate will probably depend on the molecular size of the dye. The overall effect will therefore be that the critical regain will depend on the molecular size of the dye, which again is the effect found for Fibro and continuous-filament viscose rayon.

For channels of rectangular cross-section the situation is different in its details, but not in its overall effects. In this case, for any given channel there is a particular R.H. above which it is flooded and below which it is empty. There will therefore be a sudden emptying of the channel as the R.H. passes through the critical value. As long as the channel is flooded, however, there is a continuous transport of water along the channel to the uncovered area of fabric from where evaporation takes place, and these losses are made up by water diffusing into the channel from the swollen cellulose. Consideration of the movement of dye, as distinct from that of water, is then the same as for channels of V-shaped cross-section.

Migration can take place only along continuous channels containing water. In a yarn there will be many points of contact between fibres or filaments, but few lines of contact. Water held at points of contact cannot contribute to migration. In a fabric composed of fibres of smooth cross-section containing no continuous surface channels, nearly all the moisture lost during drying at regains below the saturation regain must therefore be lost by diffusion, either of water through the body of the fibre, or of water vapour through the gaps between the fibres. Neither of these diffusion mechanisms can transport dye in visible quantities, so migration will cease when the initial surface water has drained away. This leads to a critical regain virtually independent of the molecular size of the dye used to determine it, as found for all fibres of smooth cross-section.

It is perhaps difficult to decide which of the two mechanisms, spatial or diffusion, is the controlling factor in determining the critical regain of viscose rayon for a given dye, but the evidence is in favour of the former. Consider a non-substantive dye on a viscose rayon fabric which is laid out as described in § 2.2 at an initial regain slightly less than the critical for that particular dye. Some dye will be contained in the surface water present at that particular regain. If the factor determining the critical regain is not the spatial mechanism, this water, as it travels along the channels during drying, should carry with it the dye it contains, thus producing a slight migration of dye. This effect should be more marked for dyes with a high critical regain such as the restrained dyes used. However the cut-out of migration with respect to regain for these dyes was exceedingly sharp and took place at a regain approx. 30% higher than that for the smallest dye. This therefore suggests that it is a spatial mechanism which determines the regain at which migration ceases. However, it appears that the half-width of the channel must be at least 20 times greater than the longest dimension of the dye molecule before the latter can migrate through it. This may possibly be due to irregularities in the width of the channel, as migration will be controlled by the narrowest part.

The degree of swelling of the cellulose may appreciably alter the size of any given channel. In fact the process of swelling may possibly produce channels where none existed in the dry state, but this does not affect any of the previous arguments. Comparing the results for migration on Fibro, steamed Fibro, and cross-linked Fibro, it is seen that as the swelling (i.e. the imbibition) decreases, so does the range of critical regain found. There is only a small difference between the critical regains for Lissamine Green V on Fibro and on steamed Fibro, suggesting that the degree of swelling is controlling the *range* of critical regain. When only a small swelling was allowed, as in cross-linked Fibro, no range of critical regain was detectable, but it was found that Lissamine Green V did not penetrate the fibres in this case. Hence the expected range of critical regain is small, being equal to the difference between the amounts of surface water present after centrifuging, as

estimated using Lissamine Green V and a dye restrained with Albigen A (see Table I), but these two estimations gave the same result within experimental error. This perhaps suggests that the channels postulated for the movement of Lissamine Green V are not present at low degrees of swelling.

4.6 RATE OF DRYING

For the hypothesis of transport along surface channels in viscose rayon to be tenable, it must be shown that the channels postulated are capable of transporting water at the rate required by the rate-of-drying results. It must be emphasised that the following calculations are only approximate, as they deal with an idealised system which is amenable to simple mathematics, and that they are designed simply to arrive at an order of magnitude. It may be shown (see Appendix) that the rate of flow along a parallel-sided channel under surface tension forces is given by—

$$\frac{2\gamma h r^2}{3\eta L}\ \text{c.c./sec.}$$

where—

γ = surface tension of the liquid
h = depth of channel
$2r$ = width of channel
η = viscosity of the liquid
L = length of channel.

Not all the water lost from the open end of a channel will have travelled the whole length of the channel, as the loss will be made up by diffusion through the sides along the whole length, giving a gradual increase in flow as the outlet is approached. However, L in the experiments may be taken to be 1 cm. approx.

The conditions used in deriving the expression above are not found in practice until the channels in the fibres in the uncovered area of fabric are empty. This condition is satisfied after 2 hr. of drying (see Fig. 2). The value of r at the regain which obtains at this time (58% for Fibro) may be calculated as in §4.3 to be 675 A. approx. Therefore—

L = 1 cm.
r = 6.75×10^{-6} cm.
h = 5×10^{-5} cm. (say)
γ = 72 dynes/cm.
η = 10^{-2} poise.

Giving rate of transport/channel = 1×10^{-11} g./sec. approx.

This is equivalent to 2% regain/hr. per channel for a fibre of 1·5 denier, or approx. 10% regain/hr. if the fibre contains 5 surface channels.

The drying rate of the covered portion of the Fibro fabric at 58% regain was 5·75% regain/hr., whilst that of the M95 fabric after the same time of drying was 3% regain/hr. The difference in these two rates, which should give approximately the rate of transport along the channels, is 2·75% regain/hr. It therefore appears that the channels postulated for normal viscose rayon are quite capable of transporting dye in visible quantities at the rate required by the drying results. In fact the calculation suggests that the controlling factor in the rate of transport may be the rate of evaporation at the open end of the channel.

4.7 THE AMOUNT OF SURFACE WATER PRESENT ON VISCOSE RAYON AS A FUNCTION OF REGAIN

An effective value of r at the imbibition value may be obtained by plotting r against regain and extrapolating. A better extrapolation, however, is that of the plot of log r against log regain, which is approximately linear. This gives the value r = 3,600 A. approx. at the imbibition value.

The area of the part of the cross-section of a V-shaped channel filled at any given R.H. is proportional to r^2, provided that the angle of the V remains constant, the actual value of this angle being immaterial. Assuming that the channel size distribution is equivalent to the filling of V-shaped channels and that 10% surface water is present when r = 3,600 A. at the imbibition value of 83% regain, it is possible to calculate the amount of surface water present at any other regain from the corresponding value of r as given in Table II. The results of this calculation are given in Table III, illustrated by Fig. 10. This curve suggests that surface water is not present below a regain of about 40%.

TABLE III

Regain (%)	Surface Water Present (%)
83	10·0
75	3·6
71	1·5
65	0·7
60	0·4
52	0·15
50·5	0·10
45·5	0·04
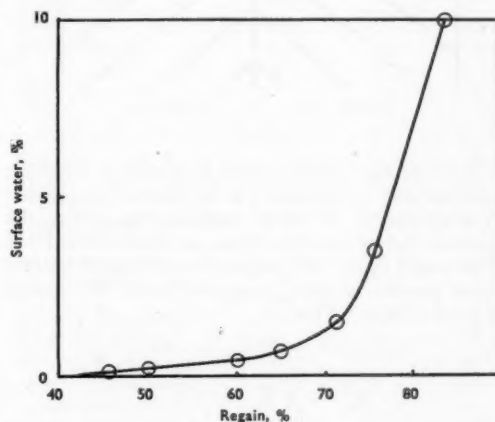
FIG. 10— Surface Water as a Function of Regain for Viscose Rayon

4.8 THE DEGREE OF MIGRATION AS A FUNCTION OF REGAIN

It is seen that Fig. 1, illustrating the pattern of migration on a Fibro fabric at different regains, shows that for Lissamine Green V nearly all the dye was removed from the central part of the covered area when the initial regain was 70%. As the critical regain was found to be 45%, the movement of 25% regain has transported dye originally contained in 70% regain. It will next be shown

that this is possible only if the substantivity ratio $X = D_\varphi/D_\sigma$ is less than unity, where—

D_φ = concentration of dye inside the fibres (g./litre water absorbed)

D_σ = concentration of dye in the bulk solution (g./litre)

Let—

R = regain of the fabric = mass of water per g. of dry fabric

R_0 = initial regain of the fabric

M_φ = mass of dye in fabric of 1 g. dry weight

M_0 = initial mass of dye in fabric of 1 g. dry weight

X = substantivity ratio for the dye.

In this system, water inside the fibres is in equilibrium with water outside the fibres. For regains between the imbibition value and the critical regain the water outside is "surface water". It is assumed that the substantivity ratio between the dye in the surface water and in the fibres is the same as that for dye in the bulk solution and in the fibres, and also that this substantivity ratio is independent of regain between the limits of the imbibition value and the critical regain (Fig. 11).

Imbibition value $> R >$ critical regain

FIG. 11

If dR of the surface water is removed, together with the dye it contains, i.e. by migration and not by evaporation, it will be replaced by approx. dR from the interior of the fibres, as from Table III it is seen that below 70% regain the change in surface water present is small compared with the change in total regain. Then—

$$- dM_\varphi = - dR \, D_\sigma = - dR \frac{M_\varphi}{R} \frac{1}{X}$$

$$\therefore \frac{dM_\varphi}{M_\varphi} = \frac{dR}{R} \frac{1}{X}$$

As $M_\varphi = M_0$ when $R = R_0$, this gives—

$$\log \frac{M_\varphi}{M_0} = \frac{1}{X} \log \frac{R}{R_0}$$

or $M_\varphi/M_0 = (R/R_0)^{\frac{1}{X}}$

As $R < R_0$, $M_\varphi/M_0 < R/R_0$ only if $X < 1$, i.e. the fraction of dye migrating on the fabric can be greater than the fraction of regain migrating only if $X < 1$.

The substantivity ratios of the dyes used were determined at room temperature at the concentrations used in the migration experiments, and are given in Table IV.

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TABLE IV

Substantivity Ratios at 20°C.

Dye	Fibro	Fabric M95 Staple	Cotton
Lissamine Green V	0·3	0·2	0·6
Azo Geranine 2G	1·5	1·3	—
Solway Blue BN	0·9	—	—
Coomassie Blue RL	1·7	—	—
Carbolan Blue B	0·35	—	—

</div>

For Lissamine Green V on Fibro at an initial regain of 70%,

$X = 0·3$

$R_0 = 70\%$

$R = 45\%$ (the critical regain)

giving—

$$M_\varphi/M_0 = \left(\frac{45}{70}\right)^{\frac{1}{0·3}} = 0·23.$$

Hence 77% approx. of the dye should be removed from the central part of the covered area for an initial regain of 70%. This is roughly in accordance with the experimental observations.

For Azo Geranine 2G, $M_\varphi/M_0 = (52/70)^{\frac{1}{1·5}}$ as the critical regain for this dye was 52%, giving $M_\varphi/M_0 = 0·82$, or only 18% approx. of the dye will migrate, again roughly in accordance with the experimental observations.

5. Interpretation of Previous Determinations of Critical Regain

The results of previous determinations of a critical regain found by various methods are summarised in Table V.

Most of the workers in this field have identified their critical regain with the saturation regain, i.e. that at 100% R.H. Some [15] even suggest that their method is the best available for determining the saturation regain. However, the experiments have

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	Migration [16]	Rate of Drying [17]	Critical Temperature in Drying [11]	Radio-frequency Drying [18]	Non-freezing Water [19]	Present Work (Migration)
Viscose rayon	40	40	38	40	38	45–85
Cottons (various)	21	17–28	26	28	17·5	31
Dicel	—	—	—	—	19	19·5
Wool (various)	36	—	39	35	38	46
Nylon	10	7·4	—	7	10	—
Glass	<3	—	—	2	—	—
Fortisan	—	30·4	—	40	—	—
Silk	—	—	27	30	40	—

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The interpretation which must be put on the previous determinations is now a little clearer. For viscose rayon, there is some "liquid water" present outside the geometrical outline of the fibres down to a regain of about 40%. This does not mean, however, that all water in excess of 40% regain is in the liquid state. The water present in channels at, say, 45% regain (desorption) will have been truly imbibed water when the regain was 80%, and will have diffused into the channel only as the original surface water was removed.

The latest paper on the determination of critical regains, by Preston and Tawde [19], is concerned with the freezing-point depression in assemblages of moist fibres. It was found that there was no detectable freezing point in viscose rayon with a regain of less than 40%, and it was therefore concluded that the "bound water" in saturated viscose rayon amounts to 40% regain. This conclusion is now seen to be incorrect. According to the present hypothesis, the amount of water freezing at 0°c. in saturated viscose rayon is the surface water, which amounts to only a few per cent regain, and not to the difference between 40% and the imbibition value. It is interesting to note that Preston and Tawde's results show that the freezing point of water in viscose rayon drops below 0°c. when the regain drops below 85%, and falls with decreasing regain until at 40% it becomes non-existent, thus showing that the water freezing at regains below 85% has a reduced activity, in accordance with the present hypothesis. The absence of a freezing point at regains below 40% merely implies that at this regain the surface water has completely disappeared from the channels.

6. Conclusions

The hypothesis is advanced that the range of critical regain in migration found for normal viscose rayon and Fibro can be explained by the presence of small continuous channels running along the length of the fibres. These channels are probably in the indentations between the lobes of the fibres.

As the humidity of the surrounding atmosphere is increased, water is absorbed by the body of the cellulose, and at very high R.H. small channels also become flooded. As the R.H. is increased still further up to saturation, more water is absorbed into the interior of the cellulose and larger channels become flooded, an equilibrium always being maintained between the imbibed and surface water. Although these flooded channels are capable of transporting a large amount of water, the amount they actually contain at any time is small. When all the channels are flooded, i.e. at 100% R.H., the amount of water held outside the geometrical outline of the fibres will be close to that measured by means of a dye-restrainer complex which does not penetrate the fibres. This amounts to approximately 8–10% regain for a typical viscose rayon or Fibro fabric with an imbibition value of 80–100%.

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Material	Total Imbibition (%)	Surface Water (%)	Estimation of Saturation Regain (%)
FIBRES AND YARNS			
Fibro, 3 denier, 2½ in.	102	7	95
Viscose rayon, 200/40	103	6	97
Viscose rayon, 150/100	114	8	106
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Nylon, 45/15	13·9	3·2	10·7
Terylene staple, 4 denier, 2½ in.	7–10	8·5	<1·5
Orlon, 3 denier, 2½ in.	18–22	12	6–10
Fibrolane, 4½ denier, 6 in.	80	4	76
Cotton (raw Sao Paulo, 3⁰⁄₃₂ in.)	64	16	48
Cotton (raw Peruvian Tanguis, 1³⁄₃₂ in.)	62	22	40
Merino wool, 64s	38·5	3	35·5
Glass, 50/60	7·5	7·5	0
FABRICS (from Table I)			
Fibro (I)	83	9	74
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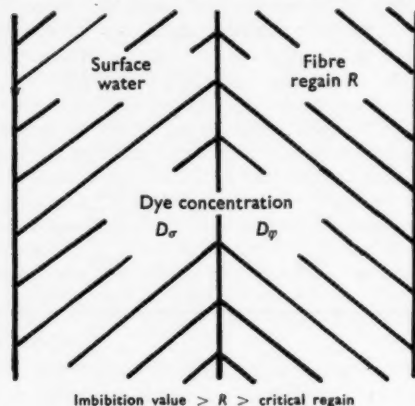

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1½ denier, 1 7/16 in., spun to single 32s
Plain weave, 84 ends/in., 59 picks/in.

(2) M95 and Toramomen staple, cotton (American) and Fibro (II) untreated, steamed, and cross-linked $1\frac{1}{2}$ denier, $1\frac{7}{16}$ in., spun to single 18s
Plain weave, 66 ends/in., 55 picks/in.

(3) Continuous-filament viscose rayon
Plain weave: Warp— 75/75, 116 ends/in.
             Weft— 75/75, 100 picks/in.

(4) Continuous-filament Dicel
Plain weave: Warp— 75/19, 200 ends/in.
             Weft— 200/38, 62 picks/in.

(5) Wool
2/2 Twill: Warp— 2/22s, 46 ends/in.
           Weft— 2/20s, 40 picks/in.

CALCULATION OF THE RATE OF FLOW ALONG SMALL CHANNELS

Consider a channel of rectangular cross-section, open along the top and at one end, supplied at the other end by a reservoir of liquid at zero hydrostatic pressure (Fig. 12). Let the R.H. be high and constant for a length L along the channel, and then decrease over a length l to room R.H. Assume that $L \gg 1$.
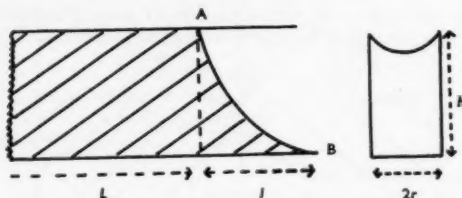

FIG. 12

Whatever the shape of the surface AB, the surface tension forces acting along the length of the channel will be—

$$2h\gamma + 2r\gamma$$
$$\text{or } 2h\gamma \text{ if } h \gg r.$$

This is equivalent to a pressure acting on the liquid in the channel equal to—
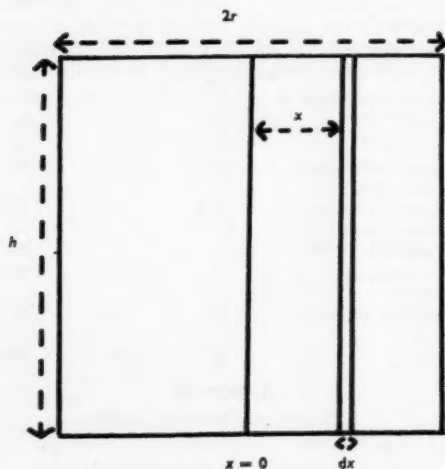
$$\frac{2h\gamma}{2hr} = \frac{\gamma}{r}$$

FIG. 13

If $h \gg r$, the liquid will flow along the channel with streamlines parallel to the longer sides (Fig. 13).

Equating viscous forces acting over the element dx for a length L with the pressure due to surface tension forces, then—

$$-\eta \frac{du}{dx} hL = \frac{\gamma}{r} hx$$

where u is the velocity of the liquid at x and η is the viscosity of the liquid, i.e.—

$$-du = \frac{\gamma}{\eta Lr} x \, dx$$

when $x = r, u = 0$

$$\therefore u = \frac{\gamma}{2\eta Lr} (r^2 - x^2)$$

The volume dV flowing per second through the element is given by—

$$dV = h \, dx \, u$$
$$= \frac{\gamma h}{2\eta Lr} (r^2 - x^2)dx$$

Hence the total volume per sec. flowing through the channel—

$$= \int_{-r}^{+r} dV$$
$$= \frac{2\gamma h r^2}{3\eta L}$$

*   *   *

The author wishes to thank Miss J. Hall for carrying out the often-tedious experimental work involved.

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EXTERNAL ADDRESSES

The Application of Reactive and Direct Dyes to Rayon Staple by Continuous Methods*

R. C. CHEETHAM

The principles of continuous piece dyeing have been studied, and an investigation has been made into the possible application of these principles to viscose staple fibre, with particular reference to dyeing for the carpet trade, where large weights to a colour are often called for.

Various machines capable of conveying staple fibre in a continuous manner have been considered, including the necessary machines for opening, dyeing, squeezing, steaming, and drying. Development work over the past two years has resulted in one continuous dyeing system based on the Fleissner revolving drum principle. This machine is now operating on a commercial scale with 15-denier crimped Fibro for use in tufted carpets. An alternative dyeing system based on the Callaghan machine for bonded non-woven fabrics is also being developed, and attention has been given to the possibility of using scouring bowls.

It has been demonstrated that reactive dyes can be applied satisfactorily in continuous systems, using the method whereby the fibre is impregnated with dye–alkali mixture and dried; only the cold-dyeing members of the Procion range have been applied commercially. Direct dyes have also been applied successfully, mainly on the Fleissner system, and in order to obtain efficient penetration and the required fastness standards, the method has become essentially short-term dyeing followed by simultaneous steaming and drying.

The application of direct dyes to Fibro in continuous systems has been studied in some detail, with main emphasis on the measures to be taken to ensure regularity of colour over a long run. This is particularly important in view of the large proportion of dye absorbed by the fibre during immersion in the dye liquor. Several methods have been examined for means of arriving at the necessary adjustments to the feed liquor; one promising method relies on spectrophotometric estimation of the dye removed from a sample of fibre initially dyed to the required colour.

Wet fastness of fibre dyed in these continuous systems is in some cases lower than that obtained by normal methods of dyeing, but adding salt or increasing the temperature of impregnation minimises the disparity.

Fibro dyed on the Fleissner system has been subsequently processed to yarn on the modified cotton and on the woollen systems of spinning. No particular difficulties have been encountered and the fibre is more lofty than when dyed in enclosed machines.

The position of dyed fibre in relation to mass-dyed fibre has been discussed. It is thought that the two methods of colouring will be complementary.

Introduction

The wet processing of textile materials by continuous means is a worthwhile objective if the following requirements can be met—

(1) Relatively large weights for processing in a particular manner

(2) Fastness in the case of dyed goods equivalent to normally accepted standards

(3) Satisfactory performance of the processed material in subsequent operations.

The advantages of a successful continuous process are both economic and technical, since in addition to high output with low labour costs, one might expect uniformity of colour over a large mass and advantages in subsequent processability due to greatly reduced exposure to wet processing conditions.

It seems probable that continuous dyeing could now be extended to staple fibres in appropriate fields. One such field is the carpet trade, with a large consumption of dyed staple fibre for plain ground colours of conventional carpets and for tufted carpets.

Continuous Processing of Textiles

Bleaching and scouring of cloth are well known examples of continuous processing, whilst in the dyeing field cloth has again received most attention, and methods such as the Standfast molten metal, du Pont pad–steam, etc., are now becoming established.

The continuous dyeing of cloth is based mainly on a short immersion time in a relatively small volume of dye liquor, whereby dye solution is absorbed, excess removed by squeezing, and the dye then fixed by heat transfer from molten metal, steam, oil, or other means. During these operations little or no migration of dye takes place and, indeed, levelness of colour depends largely on this fact, as distinct from a normal dyeing, where levelness is associated with the movement of dye molecules, equilibrium being reached over a relatively long period.

Whilst the same principles of dye absorption and fixation apply equally well to staple fibre, the indeterminate physical state of a fibre lap presents greater technical and mechanical problems in dyeing and conveyance. For example, heat transfer throughout a fibre lap during steaming or drying usually takes longer than is the case with cloth, and a similar consideration applies to dye fixation, whilst mechanically it is much more difficult to convey fibre through a continuous system.

The machinery described in this paper has therefore been either specially designed or modified from conventional equipment to meet the particular requirements of a continuous dyeing system for staple fibre. Most of the development work has been concerned with Fibro, mainly in 8- and 15-denier matt crimped fibre, as used in the carpet trade.

Machinery for the Continuous Dyeing of Fibro

The most convenient form of staple fibre from the point of view of conveyance and even treatment is a lap such as may be formed during the normal processing of textile fibres. The conventional hopper feed may, if necessary, be augmented by other means designed to produce a lap of well opened fibre of consistent thickness. The lap-forming unit of a machine for manufacturing non-woven fabric is a further possibility. Whatever method is employed, it is desirable to produce a lap of predetermined dimensions in order to have control over the liquor ratio.

Several methods of conveying staple fibre through a dyebath have been considered, including a revolving drum and double endless mesh belts. After immersion in dye liquor, the fibre must be removed by conveyor belt and passed through squeeze rollers to express surplus liquor, which should flow back to the dyebath. It is desirable to aim at a high degree of expression (of the order of 100%, i.e. with the fibre retaining only its own weight of dye liquor), so as to reduce to a minimum any migration of dye as the fibre undergoes further processing. The squeeze head may combine both hard and soft rollers, of either metal or rubber, and a convenient control of pressure should be provided.

Fixation of dye often entails steaming, and it may be advantageous to have a stage of preheating, partial drying, or incubation to facilitate even treatment and produce maximum fixation and fastness. The dyed fibre may be given an opening treatment to improve drying, but care must be taken to keep fibre breakage to a minimum.

Drying can be carried out on the conventional brattice or around revolving drums, and the fibre on delivery should be in a satisfactory state for further processing, usually into yarn. It may be desirable to ensure also that the fibre is delivered cool and suitably conditioned.

SUMMARY OF METHODS FOR ADAPTING TEXTILE-PROCESSING MACHINERY TO CONTINUOUS DYEING

Mainly existing machines used for processing staple fibre to yarn and for scouring and drying have been considered, as well as the necessary modifications made to accommodate the application of the appropriate dyes to Fibro in the form of a fibre lap. In close collaboration with Maschinenfabrik Fleissner & Sohn, Egelsbach, near Frankfurt/Main, West Germany, the revolving-drum principle already in existence for drying and for scouring was adapted and embodied in a range of machines for the dyeing and finishing of Fibro staple. An alternative method is being developed with the assistance of Messrs. A. E. Callaghan & Sons Ltd. (Birfield Engineering Group): it is based on existing plant intended for the manufacture of bonded non-woven fabrics. The fibre lap is passed between two endless mesh belts through a dyebath formerly used as the impregnation bath for bonding media.

Conventional wool-scouring bowls normally used for either raw wool or yarns have also been considered, in view of their present use for continuous processing. Although initial trials have been

carried out with limited success, the incorporation of scouring bowls in a continuous dyeing system for viscose rayon staple requires much more development work.

DETAILED DESCRIPTION OF POSSIBLE CONTINUOUS SYSTEMS FOR THE DYEING OF FIBRO

(a) Fleissner System

The sequence of machines is illustrated in Fig. 1; a brief description has appeared elsewhere [1].
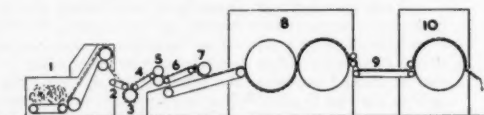
1 **Hopper feed of conventional type.**
2 **Conveyor belt to dyeing unit.**
3 **Drum dyeing machine,** consisting of a tank in which revolves a steel drum covered on the circumference with a fine mesh. Liquor is circulated by means of a pump with the propeller head situated just inside the drum. The pump serves the dual purpose of circulating dye liquor and causing the fibre to be held by suction to the outside of the drum as the latter revolves through the dye liquor.
4 **Conveyor belt to squeeze rollers.**
5 **Squeezing head,** which is pneumatic-hydraulic with an upper rubber roller and a chromed steel lower roller fluted to allow better intake of the wet staple fibre.
6 **Conveyor belt to picker.**
7 **Picker for opening the squeezed fibre.**
8 **Drier,** consisting of revolving drums with a fan in each drum, and providing for steam injection so that the unit can become a "steamer-drier".
9 **Conveyor belt to cooler.**
10 **Further revolving drum fitted with fan to draw cold air through the dried fibre.**

FIG. 1— Fleissner System

Additional items include storage tanks for dye and chemical solutions, the contents of which are pumped along feed lines to the dyeing unit. The level of the dye liquor is controlled by a constant-level device, and the temperature is thermostatically controlled. The dyeing unit is illustrated in Fig. 2.

FIG. 2— Fleissner Dyeing Unit

(b) Callaghan System

The Callaghan range is illustrated in Fig. 3 and consists of the items listed below.

In the Callaghan system provision can be made for including a pad-forming unit immediately before the dyeing machine. The unit consists of a trunking along which the opened fibre is blown by

I Hopper feed of conventional type.

2 Pre-opening unit consisting of a cylinder (of diameter 17 in.) of the spiked pin or metallic wound type.

3 Conveyor belt.

4 Endless belts to convey fibre through dye liquor.

5 Dyeing machine consisting of the former impregnation unit for applying bonding media in the manufacture of non-woven fabrics.

6 Squeezing head No. I.

7 Conveyor belt.

8 Squeezing head No. 2.

9 Brattice drier of conventional type. The one used for trials was supplied by the Spooner Drying & Engineering Co. Ltd.

Fig. 3— Callaghan System

means of a centrifugal fan to collect in the form of a lap at a set of condensing rolls. These rolls are adjustable for nip, from contact to 6 in. spacing, depending on the weight and the nature of the required lap [2].
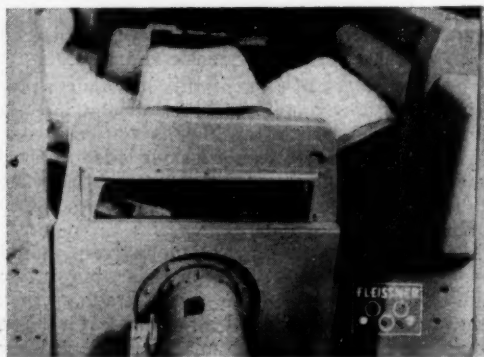
This unit is capable of forming a regular compact lap of well opened fibres intended for non-woven fabrics. In certain circumstances this process may result in excessive fibre breakage, so for continuous dyeing it may be replaced by the simpler sequence of operations indicated in Fig. 3.

(c) Use of Raw-wool Scouring Machines

Some attention has been given to the use of a scouring range for continuous dyeing. At first sight, such a method has possibilities, since a scouring range is already providing a means of conveying material in a continuous manner. It is known, moreover, that scouring bowls are being used in the United States for dyeing loose wool with metal-complex dyes, apparently successfully. Such a method has been described by Lemin in a recent paper on continuous methods [3].

A trial has been carried out on a raw-wool scouring machine fitted with a harrow, but the high liquor ratios create difficulties when dyeing cellulosic fibres in anything but very pale colours. The conveyance of the wet fibre is not very satisfactory, nor are the squeezing arrangements suitable for Fibro. It is possible that raw-stock scouring bowls would be suitable if means were provided for carrying the fibre rapidly through the dye liquor, and squeezing was made more efficient so as to give consistent expression.

(d) Petrie & McNaught Yarn-scouring Machine

An experimental machine was used. It was originally intended for more efficient scouring of woollen and worsted yarns and is shorter than the conventional yarn-scouring range. It has over-head delivery of liquor by shower from tanks erected above a brattice, the liquor being returned by a circulatory system. Preliminary trials with cold-dyeing Procion dyes have been carried out in this machine with limited success. The relatively long exposure of fibre to dye liquor suggests that this machine would be more suited to dyeing than to padding.

Dyes for the Continuous Dyeing of Fibro

Reactive dyes, because of their molecular structure and method of application, are well suited to simple impregnation techniques. In practice, only the cold-dyeing Procion (ICI) dyes have been used for Fibro in the continuous dyeing systems described. These dyes have been particularly recommended for continuous dyeing [4]. Procion H (ICI), Cibacron (Ciba) [5], and Remazol (FH) [6] dyes have received little attention as yet for application to viscose rayon staple by continuous means, mainly because of the more prolonged periods required to effect fixation. It may also be necessary in certain instances to employ higher temperatures and more strongly alkaline liquors. It is not envisaged, therefore, that these latter types of reactive dyes could be applied to Fibro in the systems already described. Nevertheless, it is not impossible that extended systems could be set up to accommodate the particular properties of these dyes. Fixation of cold-dyeing Procion dyes either takes place on immediate drying, possibly preceded by a short incubation period, or the impregnated fibre can be batched, to be followed later by drying by conventional means. In either event the dyed fibre requires washing off, unless it is convenient to proceed directly to yarn processing, in which case removal of excess dye and alkali can be combined with yarn scouring.

Direct dyes also have been used, but only limited success attends low-temperature application because of their much lower solubility, and consequently inferior penetration and levelness. The use of higher temperatures with direct dyes immediately results in appreciable dyeing, as distinct from the simple physical absorption of dye liquor which occurs in padding, so the application of direct dyes to Fibro has been considered as a dyeing operation. The use of direct dyes may entail aftertreatments designed to improve wet fastness, although in practice if the squeezing of the impregnated fibre is efficiently carried out, only dark colours are likely to require such treatment.

APPLICATION OF COLD-DYEING PROCION DYES

The advent of these dyes seemed to offer particular advantages for continuous processing since they possess—

(a) High solubility, facilitating penetration of the fibre at low temperature

(b) Low substantivity preventing actual dyeing taking place at time of immersion, the principal requirement of an impregnation process

(c) Simple chemical reactivity enabling subsequent fixation to take place

(d) Wet fastness of a high order.

Trials with Procion dyes have been conducted on all the continuous systems referred to above on 8- and 15-denier crimped Fibro. Details of some of these trials have been given by Fowler [7].

The dyes applied initially included Procion Brilliant Red 5B and a combination of Procion Brilliant Yellow R with Procion Blue 3G. In each case the dye was applied cold with sodium

bicarbonate and Lissapol N (ICI). The Fibro after impregnation and squeezing was immediately dried, encouraging results being obtained for levelness, penetration, and fastness. The actual colour yield by this method was substantially improved by raising the temperature of application to 40°c. or, alternatively, by allowing the impregnated fibre to rest cold for 30 min., or at 40°c. for 20 min., before drying. The temperature must not exceed 40°c. because of the risk of hydrolysis of the dye before it has been absorbed by the fibre. The most suitable alkali for cold-dyeing Procion dyes when applied continuously is sodium bicarbonate, as the dye–alkali liquor is relatively stable during several hours running and yet allows high rates of fixation on heating the impregnated fibre. Limited commercial runs using the dyes mentioned were successful from the point of view of regularity of colour.

Affinity Factor of Procion Dyes

In an ideal continuous process there is no affinity between dye and fibre during the actual physical absorption of dye liquor. Consequently dye liquor of the same concentration can be used continuously to produce the same colour over a long period. Dyes that are substantive to the fibre lead to changes in concentration, and variations in colour are therefore produced during continuous running. Although these substantivity effects are in general small in the case of reactive dyes, it is likely in practice that some change of colour could occur with certain individual dyes or combinations of dyes under special conditions.

In order to produce regularity of colour, the concentration of dye liquor entering the system to compensate for loss due to absorption by the fibre may have to be adjusted to allow for the effect of substantivity. This relationship between concentration of dye solution entering the system and dyebath concentration under equilibrium conditions may be expressed as "affinity factor"[8]. The value of this factor varies with individual dyes and with conditions of application. A padding process with very short immersion times could be expected to give low values for the affinity factor, and in general Procion dyes applied cold give satisfactory results.

It has been shown that, under otherwise equivalent conditions, the affinity factor—

   (i)   Is lower with viscose rayon than with cotton

   (ii)   Falls as the concentration of dye increases

   (iii)   Increases as the electrolyte concentration rises

   (iv)   Depends to some extent on running speed

   (v)   Varies with individual dyes.

Fixation of Procion Dyes

The most convenient method of fixation consists in drying the impregnated fibre immediately after squeezing, but this often results in low colour yield and, furthermore, prevents complete diffusion of dye into the fibre. Considerably increased colour yield can be obtained by first partially drying (to 40–60% moisture), then allowing a further 20 sec. or so without further reduction of moisture content, and finally completing the drying in the normal way. An average increase in colour yield of about 50% is possible by this means.

It has been suggested that preliminary heating can be effected by means of infrared radiation[4], whilst another method is to pass the fibre round a heated revolving drum, the fibre being sandwiched between the surface of the drum and an impervious covering sheet of rubber or similar material. It is also possible to obtain improved fixation by batching, the impregnated fibre being allowed to rest for periods up to 24 hr. cold or 1–2 hr. at 50–60°c., but clearly such treatment would mean intermittent processing. Steaming is another practical method of inducing fairly rapid fixation, and 1 min. at 105°c. gives satisfactory results. It should be remembered, however, that for staple fibre some time may elapse before the latter temperature is reached, particularly in the centre of the fibre lap.

Aftertreatment of Dyed Fibre

The surplus dye and alkali remaining on the fibre after fixation can be removed by rinsing and soaping, or the final treatment may be deferred until the staple fibre has reached the yarn or fabric stage, assuming that the untreated fibre can be processed satisfactorily on the appropriate spinning system. For example, it is common practice to scour carpet yarns in order to remove lubricants. Thus, Fibro dyed with Procion dyes can be converted into carpet yarn on the woollen system without scouring, in spite of the presence of free alkali and dye, and in such instances it would be practicable to defer removal of free agents until the yarn stage. As regards actual processing on woollen spinning equipment, no difficulties were encountered, and the resultant yarns, after scouring in hank, were converted successfully into tufted carpet.

APPLICATION OF DIRECT DYES

Commercial trials have been carried out successfully, mainly on the Fleissner system, with direct dyes. The fibres used have included 3-denier, $1\frac{7}{16}$ in. staple, as well as 8- and 15-denier, $2\frac{1}{4}$ in. staple, matt crimped Fibro. There seems every likelihood that a wide range of colours of adequate fastness for carpets could be obtained with direct dyes on a continuous system. A representative range of direct dyes has been examined in some detail for suitability in a continuous system with regard to fixation, compatibility, regularity of colour and fastness.

Substantivity of Direct Dyes

It was very quickly realised that, because of the high temperatures of adsorption necessary to ensure adequate solubility, levelness, and fastness, the process with direct dyes was departing a long way from the conventional padding operation, where affinity of dye for fibre during immersion is low. For example, 15-denier Fibro immersed in a solution of direct dye (5 g./litre) at 80°c. for 35 sec., squeezed to 100% expression, and then

immediately rinsed, was found to retain as much as 50% of the dye.

Fixation of Direct Dyes

A laboratory apparatus was devised for estimating fixation. It consisted of a series of boiling tubes, fitted with condensers, immersed in a salt bath. One-gram samples of 15-denier Fibro staple were placed in three tubes, each containing 1 ml. dye solution (10 g./litre) made up to appropriate volume with water to give liquor:fibre ratios of 1:1, 2:1, and 4:1 respectively. The contents of the tubes were maintained at 100°c. (simulating exposure to a saturated steam atmosphere) for 1–20 min., after which the samples of fibre were rinsed, residual liquor being collected and made up to standard volume. The dye solution concentrations were then determined by spectrophotometric readings. Results for three individual dyes drawn from S.D.C. Classes A, B, and C, respectively, are given in Table I.

TABLE I
Fixation of Direct Dyes at 100°C.

Dye	Time (min.)	Liquor Ratio 1:1	2:1	4:1
		Fixation (%)		
CLASS A				
Durazol Helio B (ICI)	1	91	77	41
(C.I. Direct Violet 51)	2	92	85	50
	4	93	81	55
	10	92	72	64
	20	92	76	59
CLASS B				
Solar Orange RGL (S)	1	61	43	21
(C.I. Direct Orange 62)	2	76	52	21
	4	81	63	32
	10	86	72	49
	20	84	80	54
CLASS C				
Chlorazol Dark Green PL	1	80	74	66
(ICI)	2	85	79	69
(C.I. Direct Green 1)	4	87	85	74
	10	87	84	77
	20	86	86	86

Table II gives in an abbreviated form fixation data for a number of direct dyes, and it can be deduced that dyes with over 90% fixation in 2 min., say, will be eminently suitable for a short-term dyeing and steaming process. Further, it seems clear that dyes fix much better in small volumes of liquor, i.e. if high expression is obtained by squeezing. Also, at low liquor ratios of the order of 1:1, steaming times > 2 min. (or > 1 min. for certain dyes) do not increase significantly the degree of fixation.

It is seen that individual dyes vary considerably in the degree of fixation under different conditions, and it can be expected that dye mixtures will present greater difficulty from the point of view of equal fixation of all the individual dyes. The influence of liquor ratio and time of immersion is illustrated for representative dyes in Fig. 4 and 5. In Fig. 5 the addition of salt is seen to increase substantially the degree of fixation, in accordance with expectation.

Chlorazol Dark Green PL (5 g./litre)
—○— 20 min.   —△— 4 min.   —□— 1 min.
Durazol Brilliant Red B 150 (3 g./litre)
—●— 20 min.   —▲— 4 min.   —▼— 1 min.
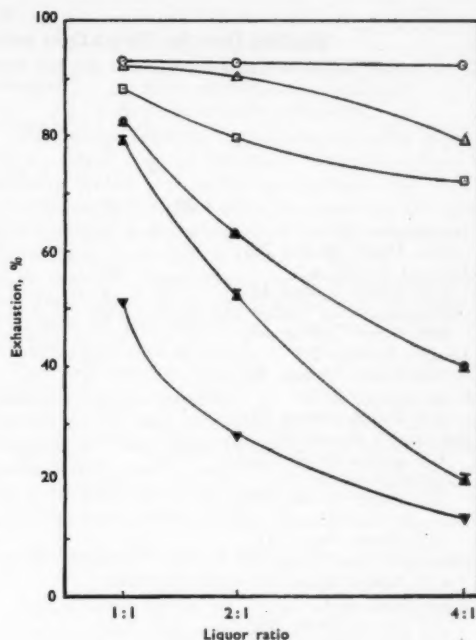
FIG. 4— Influence of Liquor Ratio on Fixation of Direct Dyes at 100°c.

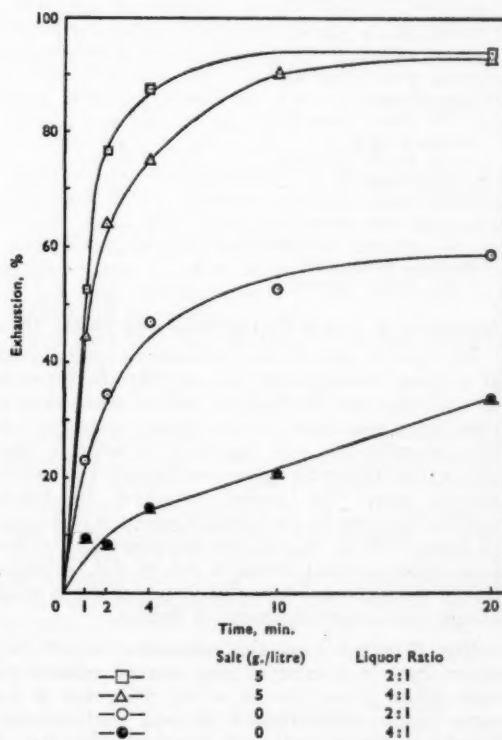|	Salt (g./litre)	Liquor Ratio
—□—	5	2:1
—△—	5	4:1
—○—	0	2:1
—●—	0	4:1

FIG. 5— Influence of Steaming Time on Fixation of Direct Dyes with and without Salt (Durazol Brilliant Red B 150, 5 g./litre)

TABLE II
Fixation Data for Direct Dyes and their Suitability for Short-term Dyeing

× indicates that the particular dye has reached at least the stipulated fixation level under the respective conditions

Dye	1:1				2:1			
	2		**4**		**2**		**4**	
	90	80	90	80	90	80	90	80
Oxyphenine 2G (C.I. Direct Yellow 28)	—	×	×	—	—	—	—	—
Durazol Yellow 4G (C.I. Direct Yellow 44)	×	—	×	—	—	×	—	×
Chlorantine Fast Yellow SL (C.I. Direct Yellow 50)	×	—	×	—	—	—	—	—
Durazol Orange 2G (C.I. Direct Orange 34)	×	—	×	—	—	—	—	×
Solar Orange RGL (C.I. Direct Orange 62)	—	—	—	×	—	—	—	—
Solophenyl Brown GL (C.I. Direct Brown 115)	—	—	—	—	—	—	—	—
Solophenyl Brown RL (C.I. Direct Brown 116)	—	—	—	×	—	—	—	—
Benzanil Fast Brown 6RL (C.I. Direct Red 111)	—	—	—	—	—	—	—	—
Chlorazol Dark Green PL (C.I. Direct Green 1)	—	×	×	—	×	—	—	×
Solar Green 5GL (C.I. Direct Green 28)	×	—	×	—	—	—	—	—
Sirius Supra Olive GL (C.I. Direct Green 23)	—	×	×	—	—	—	—	×
Durazol Helio B (C.I. Direct Violet 51)	×	—	×	—	—	×	—	×
Chloramine Pink 2B (C.I. Direct Red 75)	×	—	×	—	—	—	—	×
Chlorantine Fast Red 6BLL (C.I. Direct Red 79)	—	×	×	—	—	—	—	—
Chlorazol Fast Red F (C.I. Direct Red 1)	×	—	×	—	×	—	×	—
Durazol Brilliant Red B (C.I. Direct Red 80)	—	—	—	—	—	—	—	—
Durazol Blue G (C.I. Direct Blue 78)	—	×	×	—	—	—	—	—
Chlorazol Blue G (C.I. Direct Blue 10)	×	—	×	—	—	—	—	×
Durazol Blue 2R (C.I. Direct Blue 71)	—	×	×	—	—	—	—	—
Durazol Blue 2GN (C.I. Direct Blue 76)	×	—	×	—	—	×	—	×
Chlorazol Black BH (C.I. Direct Blue 2)	×	—	×	—	—	—	—	×

Regularity of Colour during Runs with Direct Dyes

It is known that, in any continuous system held at a given temperature, an equilibrium between dye on fibre and in dyebath will be reached in a time dependent upon volume of bath, rate at which fibre absorbs dye, and degree of expression. For direct dyes under the given conditions, the colour change over the period required to reach equilibrium may be appreciable, and it is necessary to know how to adjust the concentration of the feed liquor, so that constant colour will be maintained throughout, i.e. equilibrium conditions must obtain from commencement of dyeing.

Fig. 6 shows how the concentration of two direct dyes in a mixture may change relative to each other, giving rise to colour difference if the same liquor concentration is used continuously. In this particular example the concentration of the red component gradually becomes stronger relative to that of the violet component, so the colour becomes much redder. In this case, the feed liquor will clearly need more violet dye than red dye.

ESTIMATION OF FEED-LIQUOR CONCENTRATION

Several possible methods of arriving at feed-liquor concentration have been examined in connection with direct dyes.

(a) Comparison of Normal Laboratory Dyeing with Colour obtained under Required Conditions

This method is referred to by Schmidt [9] in connection with continuous piece dyeing with direct dyes. It is based on taking the material from the initial stage of running and matching the colour with a normal laboratory dyeing, thus obtaining an indication of the amount of dye which is actually on the fibre; this amount is then related to the feed liquor intended for continuous running.

Samples taken at intervals of 1 min. during continuous run
(No. 1-30)

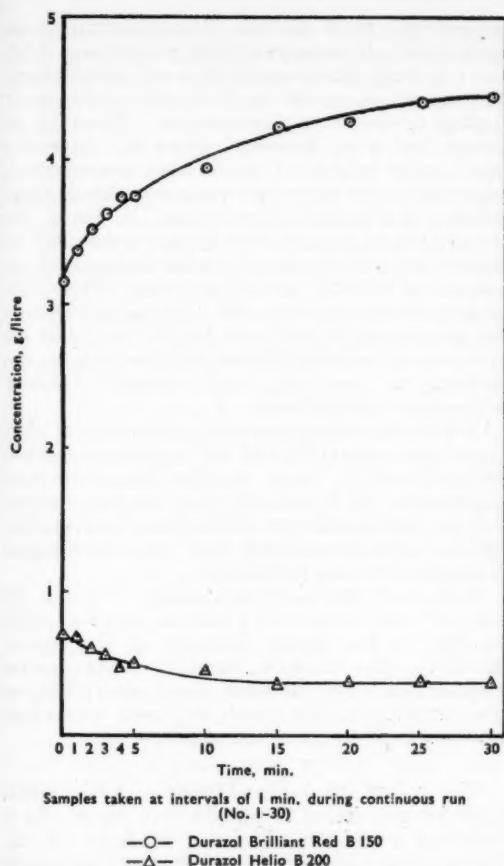—O—   Durazol Brilliant Red B 150
—△—   Durazol Helio B 200

FIG. 6—Changes in Dye Concentration in a Mixture of Two Direct Dyes during Continuous Running using the same Concentration for Feed Liquor as for Initial Dyebath

The method presupposes that all the dye is absorbed in the laboratory dyeing, either by the addition of salt or by other means, but such a degree of exhaustion is extremely difficult to attain in practice with direct dyes. Further, there is sometimes a marked difference in hue between colours produced on a continuous system and by normal dyeing. Consequently, this simple method gives only approximate guidance.

(b) *Measurement of Equilibrium and Calculation of Concentration*

A series of successive immersions is carried out with small samples in a laboratory apparatus, the volume being made up each time and each sample being compared visually with the preceding one until no apparent further change in colour is taking place, i.e. until equilibrium has been reached. The colour thus produced under equilibrium conditions is then matched under similar conditions with the first dyeing of the series, whereby two dye recipes are obtained. From these recipes the feed liquor concentration is obtained by using the empirical relationship—

$$C_F = \frac{C_A{}^2}{C_E}$$

where—

    C_A = initial dye concentration
    C_E = dye concentration at equilibrium (as given by experimental matching)
    C_F = feed-liquor concentration.

The recipe for feed liquor may be only approximate, since the calculation assumes that the affinity factor of a particular dye will not vary as conditions in the dyebath alter and that the factor remains the same when dyes are in combination, both these assumptions being of doubtful validity. The method does seem to produce acceptable results if there is no gross difference between the affinities of the individual dyes or between the concentrations of initial and feed liquors.

In practice, a further series of successive immersions is required in order to check the accuracy of the calculated recipe. Empirical corrections can then be made, following visual examination, or the equilibrium concentration can be rematched and the whole proceeding repeated until an acceptable run is established.

(c) *Estimation of Dye on Initial Sample after Dyeing under the Required Conditions*

The amount of dye on a fibre sample dyed to the correct colour under machine conditions may be determined by extracting the dye from the fibre with pyridine and analysing the solution by means of a spectrophotometer [10], e.g. a Unicam SP 600. Two 1-g. samples of fibre are each successively extracted with four equal portions of 15% aqueous pyridine. The four extracts are then combined, made up to volume, and diluted as necessary. Optical densities are measured at the wavelengths of maximum absorption of each of the dyes present.

The concentration of each of the dyes present may then be calculated, for wavelength λ_1, by solving equations of the type—

$$D_1 = K_{1A}C_A + K_{1B}C_B + K_{1C}C_C$$

where D = optical density, C = concentration of a dye, and K is a constant in each case. The constants K_{1A}, K_{1B}, etc., are obtained from the optical densities of solutions in pyridine of the single dyes at the appropriate wavelengths. Errors may be introduced if the constants are determined in aqueous solution.

For each dye the feed-liquor concentration is given by—

$$\frac{100W_D}{EW_F}$$

where W_D = weight of dye on fibre, W_F = weight of fibre, and E = expression (%) of squeeze rollers.

In the analysis of the pyridine extract the errors are normally less than 5%. Greater errors may occur when dyes have wavelengths of maximum absorption which are close together, and when the concentration of one dye is small compared with the concentration of two others in the mixture. In some cases, errors can be reduced by selecting wavelengths other than those of maximum absorption for the measurements.

General Approach

All three methods described have been tested under laboratory conditions, but limited experience

in continuous dyeing on a commercial scale has prevented full investigation. Whichever method is employed, it is inevitable that, in the laboratory, only approximate predictions can be made of the changes in colour likely to occur during continuous running, and final adjustments of dye recipes for maintaining uniform colour may have to be done on the machine itself.

It follows that the prerequisite for successful running to shade is strict standardisation of factors likely to vary, e.g. liquor ratio, temperature, time of immersion, and squeezing. These variable factors are likely to be much more important with direct dyes, since affinity for the fibre, particularly at the higher temperatures required for satisfactory solubility, is much more marked. It is advantageous to use concentrated brands of direct dyes.

In practice it has been found that the S.D.C. classification of direct dyes serves as a very rough guide to likely compatibility of dye mixtures. For example, it has been observed that combinations of Class A with Class B dyes tend to give gross variations in colour during running, as shown in Fig. 6; on the other hand, many Class B dyes can be combined with fairly satisfactory results. Some useful data have been compiled by Farbenfabriken Bayer on the effect of the substantivity of direct dyes in a padding process, with particular reference to the behaviour of dyes in mixtures [11].

FASTNESS OF DYED FIBRE

The fastness of loose fibre dyed by a continuous process has been compared with that of conventionally dyed fibre. With certain direct dyes the wet fastness is inferior, although much depends on the degree of fixation attainable in the particular system under consideration. As would be expected, wet fastness is better when absorption takes place at higher temperatures, and in practice 80°c. is recommended for direct dyes, in spite of the wider adjustments necessary to accommodate changes in colour during running.

The wet fastness of direct dyes after short immersion periods in the cold is decidedly low, particularly in darker colours, and the fastness is still further reduced by adding salt to the dyebath. The cause is thought to lie in dye aggregation, since the fastness also appears to be reduced if additions are made of those auxiliary agents which form dye aggregates that break up as the temperature rises.

Comparison of Dyed and Mass-coloured Fibres

The work of evaluating the various possible methods of continuously dyeing Fibro is proceeding with all practicable dyes, and it may be some time before final conclusions can be drawn. The economic considerations must clearly be set against quality of product, and dyed Fibro will always tend to be compared with Fibro-Duracol (mass-coloured viscose rayon staple).

Duracol colours have an undoubted advantage with regard to wet fastness, but it may well be that, for inexpensive floor coverings, high wet fastness is by no means invariably required, and experience

suggests this to be the case. If manufacturers are correct in their assessment that, over a large field, the relatively cheap direct dyes are satisfactory, then a preference for the flexibility which stock dyeing confers is understandable. There is no doubt that some Duracol colours are attractive when large weights of staple fibre are required, provided that a particular trade can absorb these weights in a limited colour range. However, the use of Duracol colours must always necessarily be limited, not only by this major consideration of the number of colours, but also by other factors concerning the holding of stocks, changing preferences for proportion of matt and bright yarn, and for crimped and uncrimped yarn, and above all, by the necessity to make very rapid changes of colour when fashion so dictates.

It will thus become necessary to ascertain at what point mass-coloration and the continuous method for stock dyeing begin to offer their respective advantages. It is probable that the two systems will be complementary rather than competitive, but the exact relationship may vary according to the industry being considered.

It is much too early to attempt to assess the value of continuous dyeing and the part it is likely to play in the dyeing industry of the future. However, the modern trend towards greater standardisation of methods would seem likely to give impetus to the search for more continuous systems at all stages of manufacture.

*   *   *

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Discussion

Mr. H. A. TURNER: The entry of fibre into the Callaghan dyeing unit using two mesh belts is reminiscent of the Brandwood machine in operation during the late 1920's for the application of sulphur

dyes to loose cotton. Is the Callaghan machine capable of the same high rate of production as was claimed for the Brandwood machine?

Mr. CHEETHAM: The Callaghan machine has been developed independently of the Brandwood machine and is intended primarily for the application of reactive and direct dyes to viscose rayon staple. As the machine is still in the experimental stage it is not possible to indicate production rates.

Mr. J. RAYMENT: Is the author satisfied that the fastness of the reactive dyes to gas-fume fading is sufficiently high to justify their use for carpets?

Mr. CHEETHAM: We have no practical experience of the effect of gas-fume fading on carpets made from yarns dyed with reactive dyes.

Mr. F. SMITH (*communicated*): A relatively short time is given for the fixation of dyes. How does this conform with times of half-dyeing?

Mr. CHEETHAM: We are studying the significance, in relation to dyeing rates and other similar phenomena, of the periods required for fixation of dyes on continuous systems. It would appear that dyes must be selected to suit the conditions existing in a particular system, and their application is not necessarily governed by existing methods of classification.

Mr. J. A. FOWLER: What are the spinning properties of the dyed fibre produced by the methods described, particularly where reactive dyes are used. With regard to direct dyes, since the process is essentially pad–dry rather than pad–steam, it would seem probable that Class A and Class C dyes, applied in the absence of salt, would yield the best results. In addition, it might be possible to boost fixation by a modification of the steaming process, or possibly by the introduction of a "delay" stage, e.g. on the J-box principle.

Mr. CHEETHAM: Fifteen-denier crimped Fibro dyed with Procion dyes on the Fleissner system has been successfully spun on the woollen system without prior scouring, since any loose dye or alkali can be removed subsequently in yarn scouring. Recent work has indicated that coarse-denier Fibro dyed with Procion dyes can be spun on the cotton system without prior washing off

provided that a suitable agent, e.g. Cirrasol FP (ICI) is added to facilitate fibre processing. Fifteen- and 8-denier crimped Fibro dyed with direct dyes is being processed satisfactorily on the cotton system for tufted carpets. With regard to the selection of dyes for continuous processing, we have had as yet only limited experience. In some cases Class A or Class C direct dyes give satisfactory results, but in general, dyes must be selected to suit the conditions in any particular continuous system. Rate of fixation in steam or hot air governs the successful application of direct dyes, and several possible modifications are being considered, but any method involving a J-box would render the process discontinuous.

Mr. S. M. JAECKEL: Dyeings of Procion Red, if crease-resisted, are much less sensitive to burnt-gas fumes   However, slight shade changes are sometimes evident on the unexposed fabric after crease-resist treatment.

Mr. H. F. STEVENSON: Has viscose rayon tow been dyed on any of the systems outlined? What effect, if any, have nip pressures and rubber hardness on the spinning properties of the viscose fibre?

Mr. CHEETHAM: Viscose tow has not yet been tried on the continuous systems described. We have not carried out any work aimed at correlating squeezing of the fibre with spinning properties, but if the dyed fibre lap is too highly compressed additional opening treatment might be necessary, which could lead indirectly to an inferior yarn due to excessive fibre breakage.

Mr. E. I. NOBLE: Has disodium hydrogen phosphate been considered as an electrolyte for the continuous dyeing of direct dyes? Its steep solubility curve might be advantageous. Direct dyes would be fixed as the cooling Fibro left the dyebath.

Mr. CHEETHAM: We have used a number of compounds similar to disodium hydrogen phosphate in continuous dyeing systems, primarily as buffering agents in the dyebath to stabilise pH and minimise reduction of certain direct dyes. We have not considered the use of such compounds from any other angle.

Reactive Dyes for Nylon*

D. F. SCOTT and T. VICKERSTAFF

Conventional dyes for nylon have suffered, hitherto, from the disadvantage that those of good fastness properties do not readily cover the chemical and physical irregularities of the fibre, whilst those which are free from these defects have relatively low fastness properties.

A new range of reactive dyes for nylon has now been developed. They are disperse dyes and can be applied in an unreactive form under acid conditions, when they possess the level-dyeing properties of disperse dyes. When the bath is made mildly alkaline, reaction occurs between dye and fibre, and a fast, level dyeing is obtained. It has been found that these dyes react both with the amine end-groups and with the amide groups in the fibre, so difficulties associated with saturation of amine end-groups are not encountered.

Rates of dyeing and fixation of the dyes have been determined both separately and in mixtures and it is shown that the dyes are compatible for dyeing as mixtures. Rate-of-dyeing curves indicate that these dyes behave as medium-to-slow dyeing disperse dyes.

As with Procion dyes when applied to cellulose, a side-reaction occurs in the dyebath, and in this case the deactivated dye remains on the fibre after the soaping treatment. Since, however, the unfixed dye has fastness properties at least equal to those of conventional disperse dyes, this small proportion can be tolerated without undue loss of fastness.

For the first time a range of dyes is available for dyeing nylon to level, attractive colours with good wet fastness properties using a simple technique and conventional dyeing machinery.

Introduction

The basic difficulty confronting any dyer, apart from light fastness and subsidiary requirements, is to obtain attractive level shades having good fastness to laundering. With some fibres— and nylon is a particularly good example— these two requirements are to some extent opposed. Dyes which give level dyeings on nylon have merely moderate fastness properties; those which have good fastness are apt to show barriness— distinct light and dark streaks in weft or warp directions. The reasons for this are well recognised. Barriness arises from the difficulty of manufacturing and preparing nylon fibre in a completely homogeneous condition, both chemically as well as physically.

The chemical variation lies in the proportion of free amino groups to the remainder of the molecule, and is essentially a molecular weight factor[1]. The physical differences arise largely in the spinning and heat setting processes. Although there are indications[2] that chemical differences may eventually be reduced to an innocuous level, it would appear that physical differences (which are not, of course, confined to nylon) are likely to remain a problem. As would be expected, amine end-group differences affect only those dyes with affinity for such groups, e.g. acid dyes, whereas the physical differences influence all types of dyes to a greater or a lesser degree.

Disperse dyes are unaffected by chemical variation and relatively little affected by physical variation. The original problem remains, however: the levelling dyes have only moderate wet fastness properties, whilst dyes with reasonably good fastness properties show barriness. This dilemma is placed in perspective when it is remembered that, although at the present time by far the greater proportion of continuous-filament nylon is dyed with disperse dyes, there is continuous and increasing commercial demand for the use of faster dyes[2].

There have been many attempts to solve this problem by applying acid dyes in a level manner. One obvious approach is to employ a continuous dyeing process, in which the dye is applied by padding and then fixed *in situ*, but little success appears to have attended such efforts[3-7]. An alternative approach has been to apply acid dyes from extremely dilute dyebaths by using drip feed, almost insoluble metal salts of the dyes[8], or insoluble complexes of the dyes with cationic agents[9]. The use of special agents to promote the levelling of acid dyes has also been tried[10,11]. Finally, the use of swelling agents[12] or high-temperature dyeing to open up the fibre structure and so overcome physical differences has been advocated[2,13-15]. None of these methods has proved entirely successful, and the need still remains for fast dyes which have the same ability to cover fibre irregularities as have disperse dyes.

The success of reactive dyes applied to cellulose fibres inevitably suggested a further line of attack. Procion dyes do not, of course, provide the answer, since, being anionic they suffer from the same defects as acid dyes, but the high degree of washing fastness shown by Procion dyes on nylon encouraged further investigation.

What was clearly needed was a dye without ionic solubilising groups, capable of dyeing in the same level manner as a disperse dye and capable of becoming reactive when inside the fibre. Insertion of a chemically reactive group into a molecule of a disperse dye is relatively simple. It is highly desirable, however, that the resultant molecule should retain the advantageous properties of a disperse dye, and this, together with the retention of other desirable properties, is by no means easy to achieve. Investigation of these requirements has now resulted in the development of a new range of dyes— the Procinyl dyes— which are disperse dyes containing a group carrying a labile chlorine atom capable of reacting with nylon. These dyes are quite stable in water and in weakly acidic liquors under hot dyebath conditions, and dye in the same level manner as normal disperse dyes. When exhaustion has been achieved, the system is activated by addition of alkali, whereupon chemical reaction occurs between dye and

TABLE I

Comparative Resistance of Procinyl and Disperse Dyes to Propanol Extraction from Nylon

Dye	Dyeing	Dye on Fibre (%) after—	
		Washing at 85°c.	Propanol Extraction
3·3% Procinyl Orange GS	70	59	48
3·3% Procinyl Scarlet GS	77	72	60
2·5% Procinyl Yellow GS	85	81	49
3·3% Procinyl Blue RS	90	88	77
1·5% Dispersol Fast Orange G 300 (C.I. Disperse Orange 3)	95	60	0
1·5% Dispersol Fast Scarlet B 150 (C.I. Disperse Red 1)	95	44	0
7·5% Duranol Brilliant Blue BN 300 (C.I. Disperse Blue 3)	86	47	0
2·5% Dispersol Fast Yellow G 300 (C.I. Disperse Yellow 3)	93	58	0

fibre, and in this way the dyeing of fast, level, attractive shades on nylon has at last become a reality.

Evidence of Reaction with Nylon

Before discussing dyeing properties, the evidence which indicates that Procinyl dyes do react with nylon under alkaline conditions will be reviewed. The evidence is of three kinds—

(1) Nylon dyed with conventional disperse, azoic, or acid dyes can be stripped by boiling with solvents such as chlorobenzene, propanol, or aqueous pyridine. These, although excellent solvents for Procinyl dyes, do not extract them from nylon, which suggests that some force other than adsorption, mechanical retention, or salt linkage is holding the dye on the fibre.

(2) If nylon fibre, dyed with disperse dyes, is dissolved in o-chlorophenol and the resulting solution poured into propanol so that the nylon is precipitated, the dye appears in the liquid phase. If, however, nylon dyed with Procinyl dyes is treated in the same way, the dye remains associated with the precipitated nylon, even though it is normally quite readily soluble in both o-chlorophenol and propanol. If the unreactive analogue of Procinyl Scarlet G is treated in a similar manner the colour is removed from the nylon and is dissolved in the liquid phase.

(3) The colour of Procinyl Scarlet G is due to the presence of an azo group. Consequently the dye can be reduced on the fibre with sodium sulphoxylate formaldehyde and formic acid to two amine-containing end-products. If the dye has reacted with the fibre, one of the products should remain firmly anchored to the fibre and should resist extraction with hydrochloric acid. Such a "discharged" fibre can, in fact, be diazotised and coupled with a phenol to produce a new dye. If nylon is dyed with the unreactive analogue of Procinyl Scarlet G and treated in a similar manner, no colour is developed. Again this is very strong evidence that the Procinyl dye is combined with the fibre.

It is of interest at this point to show quantitatively the resistance of the Procinyl dyes to propanol extraction. Table I shows that, of the dye exhausted on to the fibre, a large proportion remains fixed, whereas with disperse dyes the dye

is removed completely. Dyeings of both Procinyl and conventional disperse dyes were also subjected to a severe washing treatment with 5 g. soap per litre at 85°c. for 30 min., and the amounts remaining on the fibre after the treatment determined. The results (Table I) show that not only the fixed, but also the unfixed, Procinyl dye has greater resistance to washing than coventional disperse dyes.

The above observations show fairly conclusively that Procinyl dyes do react in some way with nylon, but do not indicate the precise mode of attachment. This is a matter of considerable interest, since if reaction takes place only on amine end-groups the difficulties associated with saturation may again arise. However, reaction with amide groups along the nylon chain is also possible. These two possibilities have been examined.

If each molecule of dye reacts with one amine end-group, this should be demonstrable by estimating the number of amine ends left unreacted after dyeing. This has been determined by the standard method, which consists in dissolving the fibre in phenol-methanol and titrating conductimetrically with a standard hydrochloric acid solution in methanol. The amounts of dye estimated colorimetrically and the amine end-sites occupied are in good agreement up to the point at which these sites are completely saturated (Table II). Over this range of dye concentration, therefore, reaction appears to occur solely with the amine groups.

However, if the dye reacts only with primary amino groups in the fibre, a point will be reached with increasing dye uptake when no more sites will be available for reaction, and a limit will be imposed to the amount of dye retained after extraction with propanol. For a nylon containing 42·6 m-equiv. of end-groups per kg. of fibre, the maximum theoretical amount of dye which can be retained on this basis is 1·8–2·0 g./100 g. approx., but, as is seen from Table II, much larger quantities can be fixed on the fibre.

There are two possible explanations of this observation—

(a) The production of fresh primary amine sites by the hydrolysis of amide links

(b) Reaction of the dye with amide groups.

Degradation of nylon under the pH conditions used for dyeing is unlikely, since the fibre is

TABLE II
#### End-group Analysis of Nylon dyed with Procinyl Dyes

Dye applied (g./100 g. fibre)	Dye "fixed" (g./100 g. fibre)	Dye "fixed" (m-equiv./ kg. fibre) Colorimetric Estimation	Amine End-groups reacted (m-equiv./ kg. fibre) Titrimetric Estimation
PROCINYL SCARLET GS			
0·5	0·35	7·4	7·6
1·0	0·72	16·5	18·6
1·5	1·23	25·8	24·6
2·5	1·47	30·9	34·6
5·0	2·8	59	42·6
10·0	4·2	88	42·6
20·0	6·1	128	42·6
PROCINYL BLUE RS			
0·5	0·39	9·3	5·6
1·0	0·78	18·4	22·6
1·5	1·02	24·0	25·6
2·0	1·23	29·0	27·6
2·5	1·44	34·0	38·6
4·0	1·84	43·5	42·6
6·0	2·29	54·1	42·6
8·0	2·37	56·0	42·6

normally stable to alkali other than caustic alkali at elevated temperatures, and the acids required to achieve hydrolysis are either mineral acids or strong organic acids. Since degradation as judged by tensile strength and extensibility does not occur to any significant extent (cf. Table III), it can be inferred that amide hydrolysis plays a negligible part.

TABLE III
Strength of Nylon Yarn dyed with Procinyl Scarlet G

Dye applied (g./100 g. fibre)	Dye absorbed (g./100 g. fibre)	Tensile Strength (g./denier)	Extensibility (%)
0	0	5·2	26·9
0·5	0·3	4·7	23·0
1·0	0·6	4·9	28·9
2·0	1·1	5·1	25·3
5·0	2·8	4·8	26·9
10·0	4·2	4·7	25·2
20·0	6·1	4·5	25·8

Some indication of reaction between Procinyl dye and amide groups in nylon has been obtained by showing that reaction is possible between the dye and a "nylon model" compound—

$C_4H_9 \cdot NHCO(CH_2)_4 \cdot CONH(CH_2)_6 \cdot NHCONH \cdot C_4H_9$,
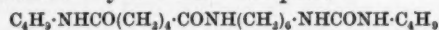
containing amides as the only reactive group. This insoluble compound was treated in a normal dyebath of Procinyl Orange G, and the coloured solid obtained was extracted with acetone, recrystallised from propanol, and treated with charcoal. The product was still coloured. When this reaction product was dissolved in propanol and the solution poured into benzene (in which Procinyl Orange G is readily soluble and in which the model compound is insoluble), the coloured solid was again precipitated and the solvent layer was almost colourless. This slight coloration is attributable to the slight solubility of the reaction product in the mixed solvent. When a mechanical mixture of

Procinyl Orange G and the model compound was similarly treated, the dye remained dissolved in the solvent and a white precipitate of the model compound was obtained.

Additional evidence for reaction has been obtained by measuring the rate of hydrolysis of the dyes in aqueous liquors—

(a) In presence of alkali and hexamethylenediamine at pH 10

(b) In presence of alkali and NN'-dibenzoyl-hexamethylenediamine at pH 10

(c) In presence of alkali only at pH 10.

For each dye the rate of hydrolysis was slightly greater (10–20%) in presence of NN'-dibenzoyl-hexamethylenediamine than in water, and in presence of hexamethylenediamine itself it was very much greater.

Taking these two types of experiment together, it is inferred that Procinyl dyes do react, under alkaline conditions, with amide groups in nylon, at a rate considerably less than the reaction rate with free amine groups. This accounts both for the stoichiometry of the reaction with amine groups shown in Table II and for the fact that reaction continues to take place after the amine groups are saturated. As the saturation point approaches, the rate of dyeing, now associated chiefly with amide groups, should be reduced from the high rate associated with the amines. Fig. 1 shows that this is so.
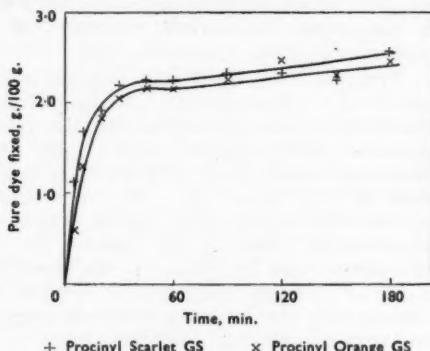
FIG. 1— Rate of Fixation of 50% Shades

+ Procinyl Scarlet GS   × Procinyl Orange GS

Dyeing Properties of Procinyl Dyes

Like other types of reactive dyes, Procinyl dyes undergo a side-reaction with water, and to minimise this it is desirable, as with Procion dyes on cellulose, to absorb the dye on to the fibre initially in an unreactive form. However, the main advantage to be gained in this manner is in terms of levelling rather than degree of fixation. With Procion dyes on cellulose the preliminary absorption may be brought about by adding electrolyte to the neutral dyebath followed by the addition of a suitable alkali. Procinyl dyes, on the other hand, are relatively insensitive to electrolyte concentration. Fortunately, however, adequate absorption takes place from acid suspensions, in which the dyes are relatively inert. This allows an efficient two-stage system to operate, by absorption of the dye in presence of acid followed by reaction in alkali.
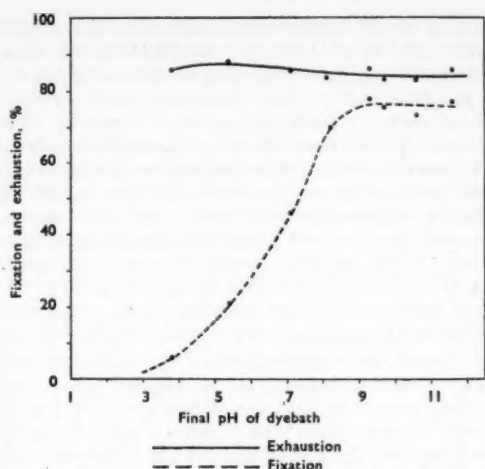
FIG. 2— Procinyl Blue RS: Variation of Exhaustion and Fixation with Dyebath pH (1% Shade (Pure Dye), Dyed for 1 hr. at 95°C., 40:1 Liquor Ratio)

Fig. 2 illustrates the behaviour of Procinyl Blue R applied by a one-stage process from dyebaths of different pH values. Whilst the exhaustion of dye varies little with change of pH, the percentage fixation—

$$\frac{\text{Dye on fibre after extraction with propanol}}{\text{Dye in dyebath}} \times 100$$

increases sharply from about zero at pH 4 to a high figure between pH 9 and 10, and a very high proportion of the dye actually absorbed on the fibre becomes fixed at these higher pH values.

The other Procinyl dyes behave similarly, although the fixation of Procinyl Orange G and Procinyl Scarlet G (Fig. 3) starts to rise at a lower pH, does not reach so high a maximum fixation, and decreases more markedly at pH >10. This difference appears to be due to the different degrees of reactivity of the dyes with water at the higher pH values.
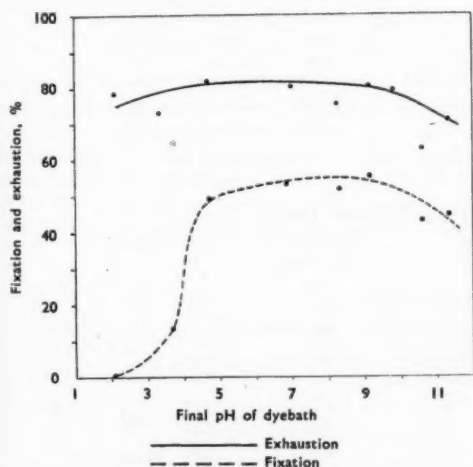
FIG. 3— Procinyl Scarlet GS: Variation of Exhaustion and Fixation with Dyebath pH (1% Shade (Pure Dye), Dyed for 1 hr. at 95°C., 40:1 Liquor Ratio)

The rate of fixation and the percentage fixation finally achieved are affected by temperature. Fig. 4 illustrates the temperature-range properties of Procinyl Blue R, the dye most sensitive to temperature. The exhaustion after dyeing for 1 hr. changes little between 70° and 95°C. The fixation at pH 9, however, rises with increasing temperature, and clearly, to achieve maximum fixation, the temperature of the dyebath should be as high as possible.
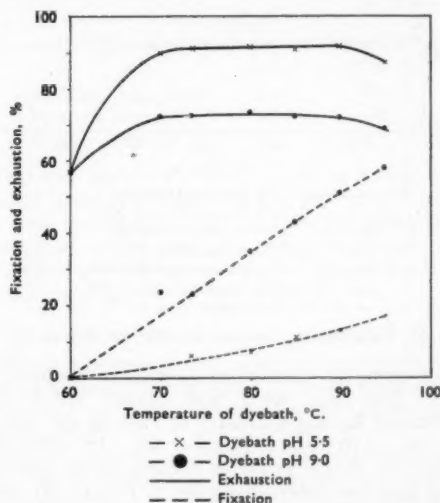
FIG. 4— Procinyl Blue RS: Effect of Temperature of Dyeing on Exhaustion and Fixation (1% Shade (Pure Dye), Dyed for 1 hr., 40:1 Liquor Ratio)

The choice of precise dyeing conditions involving a preliminary absorption under acid conditions must depend largely on the rate of decomposition of the dye in acid. It has been found that very little hydrolysis of dye occurs at pH 4 at a temperature as high as 95°C., and this, therefore, is chosen as the pH of the bath in the first stage of the dyeing process.

The advantages to be expected from the two-stage dyeing process are twofold. The first is enhanced levelling, since in the acid dyebath little fixation takes place: and the second is a higher percentage fixation. The levelling action is achieved in all cases; the increased fixation is expected only for those dyes which are relatively unstable at pH 10, and this latter effect is significant only with Procinyl Scarlet G.

RATES OF DYEING OF PROCINYL DYES IN ACID DYEBATHS

Under the conditions used in the first stage of the application of the reactive disperse dyes, they appear to act as typical disperse dyes. Rate-of-dyeing curves have been determined, using 3·3% shades, by dyeing in a buffer solution of 2 g. acetic acid, 0·25 g. ammonium acetate, and 1 g. Dispersol VL per litre. The results are illustrated in Fig. 5 and are compared with the rate-of-dyeing curves for three typical disperse dyes.

Diffusion coefficients have been determined directly by application of the Hill equation to the

Fig. 5— Rate-of-dyeing Curves for Procinyl and Disperse Dyes

3·3% Procinyl Yellow GS
3·3% Procinyl Orange GS
3·3% Procinyl Scarlet GS
3·3% Procinyl Blue RS
3·5% Duranol Red X3B 300
1·5% Duranol Violet 2R 300
3·0% Duranol Blue G 300

dyeing of nylon yarn from an infinite dyebath at 95°c. The yarn used was bright 120-denier, 40-filament having a density of 1·13, so the radius was $9 \cdot 7 \times 10^{-4}$ cm. Figures for the diffusion coefficients (Table IV) were obtained from dyeings which had been carried out for 5, 10, and 20 min., saturation values being taken as the amount of dye on the fibre after 6 hr.

The velocity coefficient k in Table IV has been derived from the equation of the hyperbola—

$$kt = \frac{1}{A-x} - \frac{1}{A}$$

where A is the equilibrium exhaustion and x the exhaustion after time t. Application of this equation to the rate of dyeing of disperse dyes on nylon gives fairly close agreement with experimental curves [16], and the same is true in this instance. The value of the velocity coefficient gives an indication of the rate at which the dyeing takes place, and, as is seen in Table IV, the values of diffusion coefficient and velocity coefficient agree well with the observed times of half-dyeing. If the values of the velocity coefficients are compared with those for disperse dyes on nylon at 95°c., it is seen that the Procinyl dyes have rate properties similar to the medium-slow dyeing disperse dyes.

It would be expected that the diffusion coefficients so far determined should be related to levelling power, so that the Blue should level to a greater extent than the Scarlet, for example. Levelling tests have been carried out in the manner described by Hadfield and Seaman [14]. The percentage levelling is expressed as—
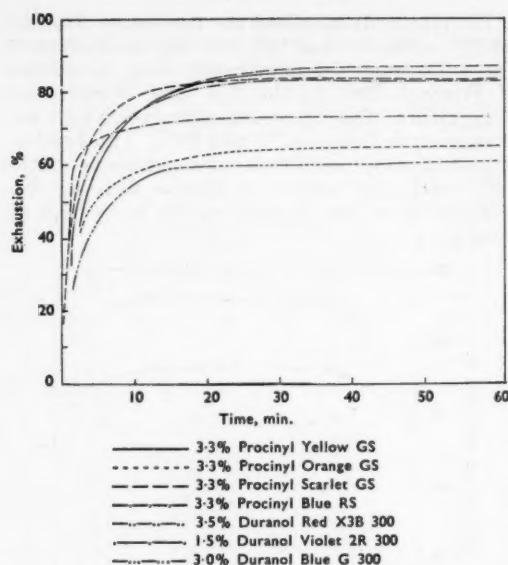
$$\frac{\text{Dye on levelled hank}}{\text{Dye on initially dyed hank}} \times 100$$

The results are given in Table V, the grading of the controls being taken from the ICI manual [17].

Procinyl Blue R and Orange G, which have almost identical percentage levelling values, have similar diffusion coefficients; Procinyl Scarlet G has a lower percentage levelling, and this is accompanied by a lower diffusion coefficient. Procinyl Yellow G, which levels to the least extent, would be expected to have the lowest diffusion coefficient, and this is indeed the case.

RATES OF FIXATION IN ALKALINE DYEBATHS

These were determined by first dyeing a number of hanks to equilibrium under acid conditions and

TABLE IV

Rates of Dyeing and Diffusion Coefficients of Procinyl and Disperse Dyes

Dye	$t_{\frac{1}{2}}$ (min.)	$k \times 10^5$	$D \times 10^{11}$ (cm.²/sec.)
3·3% Procinyl Yellow G	2	750	8
3·3% Procinyl Orange G	1·7	1010	20
3·3% Procinyl Scarlet G	1	1600	16
3·3% Procinyl Blue R	2	650	21
3·5% Duranol Red X3B 300 (C.I. Disperse Red 11)	1·7	720	—
1·5% Duranol Violet 2B 300	1	2900	—
3% Duranol Blue G 300 (C.I. Disperse Blue 26)	3·5	350	—

TABLE V

Levelling Properties of Procinyl and Disperse Dyes

Dye	Levelling (%)	$D \times 10^{11}$ (cm.²/sec.)	Grading
Procinyl Yellow G	43	8	—
Procinyl Orange G	88	20	—
Procinyl Scarlet G	75	16	—
Procinyl Blue R	87	21	—
Dispersol Fast Crimson B (C.I. Disperse Red 13)	44	—	Good
Duranol Brilliant Blue BN (C.I. Disperse Blue 3)	82	—	Good
Duranol Blue Green B (C.I. Disperse Blue 7)	60	—	Poor
Duranol Violet 2R (C.I. Disperse Violet 1)	92	—	Very good

then making the baths alkaline by the addition of sodium carbonate solution to give a final pH of 10·5 approx. The hanks were removed at various time intervals, plunged into cold acid buffer to halt reaction, and immediately extracted with propanol to remove unfixed dye. The percentage dye on the fibre was then determined by dissolving a weighed amount of fibre in *o*-chlorophenol. The curves obtained from the application of 3·3% depths are shown in Fig. 6.
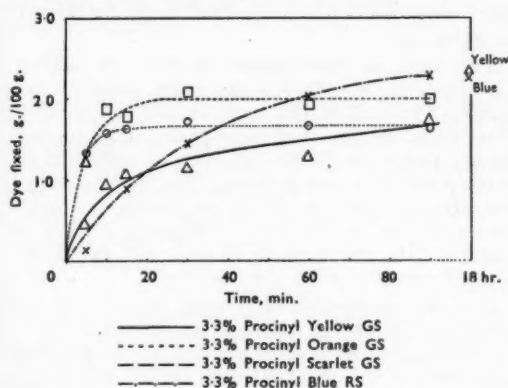

FIG. 6— Rate of Fixation of Procinyl Dyes

    ——— 3·3% Procinyl Yellow GS
    - - - - - 3·3% Procinyl Orange GS
    — — — 3·3% Procinyl Scarlet GS
    —·—·— 3·3% Procinyl Blue RS

The times of half-reaction (Table VI) indicate that Procinyl Blue R and Yellow G are much less reactive than the other two. However, the amount of dye which ultimately reacts with the fibre is governed by the degree to which it exhausts on to the fibre. For example, although Procinyl Blue R reacts much more slowly than either Procinyl Orange G or Procinyl Scarlet G, the ultimate amount of dye which reacts is greater than with the two latter dyes; this is due to its higher equilibrium exhaustion.

TABLE VI
Times of Half-reaction (min.) of Procinyl Dyes

3·3% Procinyl Yellow G	25
3·3% Procinyl Orange G	2·5
3·3% Procinyl Scarlet G	2·5
3·3% Procinyl Blue R	20

RATES OF ADSORPTION AND FIXATION IN MIXTURES

These measurements were carried out in order to determine whether the individual dyes had any mutual effect when dyed together. Two mixtures were applied, consisting of 3·3% each of Procinyl Blue R and Procinyl Orange G or Scarlet G. The results (Table VII) show that the rates of dyeing

of the individual dyes are not greatly affected by the presence of a second dye, although the equilibrium exhaustions of the Scarlet G and Orange G in the presence of the Blue R appear to be depressed slightly. It appears, therefore, that the dyes can be applied together in acid without affecting one another to any marked extent.

Rate-of-fixation curves were also determined for the dyes in the mixtures, and the times of half-reaction are summarised in Table VIII.

TABLE VIII
Times of Half-reaction (min.) of Procinyl Dyes

	Alone	In Mixture
Procinyl Orange GS	2·5	6·5
Procinyl Scarlet GS	2·5	4·5
Procinyl Blue RS	20	>25

It is seen that in all cases reaction is slower when a second dye is present. In a system where there are two reacting species of differing reactivities competing for the same site, which is present only in limited quantities, such an increase in the times of half-reaction would be expected.

COVERAGE OF IRREGULARITIES

Before discussing the practical application of Procinyl dyes, it is interesting to examine their behaviour on nylon containing deliberate gross irregularities.

In order to obtain information on the effect of large chemical differences, a sample of nylon was acetylated[1], and the absorption and fixation of Procinyl dyes on this acetylated nylon were compared with those on the control. Information on the proportions of amine end-groups in the two nylons was obtained by measuring the amount of Naphthalene Scarlet 4RS (C.I. Acid Red 18) necessary to saturate the fibre.

The amine end-content of the fibre was reduced to about one-sixth (from 42·6 to 6·9 m-equiv./kg.) by the acetylation. The total amount of dye absorbed, either in an acid dyebath or after an alkaline treatment, showed only a small reduction on the acetylated fibre, from 6·3 to 5·6 g./100 g. for Procinyl Blue RS and from 16·1 to 13·5 g./100 g. for Procinyl Orange GS, which suggests that the dyeing itself is governed by a disperse-dye type of mechanism and is little affected by chemical differences in the fibre. The amount of dye which had combined with the fibre was more markedly reduced, from 3·1 to 1·6 g./100 g. for Procinyl Blue RS and from 10·2 to 6·6 g./100 g. for Procinyl Orange GS, but even this reduction by about one-half is very much less than the difference in amine

TABLE VII
Compatibility of Procinyl Dyes

Time (min.)	Exhaustion (%) of Blue			Exhaustion (%) of Orange		Exhaustion (%) of Scarlet	
	Alone	With 3·3% Orange G	With 3·3% Scarlet G	Alone	With 3·3% Blue R	Alone	With 3·3% Blue R
5	59·8	62·4	66·6	51·6	43·3	71·2	65·2
10	74·1	74·1	72·2	57·0	50·0	78·9	68·1
15	80·0	78·2	82·6	60·1	52·1	81·6	75·3
30	84·7	83·2	84·1	62·8	57·6	82·0	77·9
45	88·0	83·8	84·6	65·2	57·7	83·8	79·1
60	86·7	84·8	85·5	66·0	59·7	84·0	78·0

end-group content. It appears, therefore, that the very much smaller chemical differences which are likely to be encountered in practice will have a negligible effect on the dyeing of Procinyl dyes.

In order to assess the coverage of large structural differences in nylon, two samples of nylon of the same amine end-group content and denier but of different draw ratio were dyed together—

(a) In an acidic dyebath

(b) In an alkaline dyebath

(c) In an acidic dyebath subsequently made alkaline

to medium depths with Procinyl Scarlet GS and Procinyl Blue RS. The results are given in Table IX.

TABLE IX
Distribution of Dyes between Nylons of Different Draw Ratio dyed in the Same Bath

Nylon A — draw ratio 3·08
Nylon B — draw ratio 3·99

Dyed at 95°c., using 40:1 liquor ratio, with Dispersol VL (1 g./litre) and buffer

Buffers— (a)   Acid bath—acetic acid (30%; 2 g./litre)
         (b)   Alkaline bath—soda ash (2·4 g./litre) added to acid bath

Dyeing Method	(Dye on Nylon A)/(Dye on Nylon B)	
	3·3% Procinyl Scarlet GS	3·3% Procinyl Blue RS
Dyed 1 hr. acid	1·12	1·08
Dyed 1 hr. alkaline	1·43	1·14
Dyed 1 hr. acid, 1 hr. alkaline	1·00	1·00

With such an exaggerated difference in draw ratio some difference in rate of dyeing would be expected; at the end of the 1 hr. dyeing period the hank with the higher draw ratio should be less heavily dyed, giving a ratio of (dye on Nylon A)/ (dye on Nylon B) greater than unity. Table IX shows results in the expected direction. In an alkaline bath the ratios are greater than in acid, whereas using the acid–alkali method both hanks are dyed equally. These results show the advantage of using the correct method of application.

The acid bath should, of course, produce less differentiation than the alkaline bath, since migration and levelling can occur more readily in acid. It is significant that the ratio in the alkaline bath is greater with Procinyl Scarlet GS, which has the higher rate of fixation, than with Procinyl Blue RS. The longer total dyeing time (2 hr.) for the acid–alkali method allows the two hanks to reach equality, since the fixation is not immediate, and some migration can occur in alkali.

Again, the difference in draw ratio in these experiments is very much greater than would be encountered in practice, and these experiments therefore give assurance that coverage of barriness will be achieved in practice through the application of Procinyl dyes by the acid–alkali technique.

Practical Application of Procinyl Dyes

The practical application of Procinyl dyes to continuous-filament nylon and nylon staple may be accomplished both by batchwise dyeing and by printing. They may also be applied usefully to a number of other fibres.

6,6-NYLON
Batchwise Dyeing

The dyes are first applied at 95°c. from an acidic bath containing 2 parts acetic acid (30%) and 1 part of Dispersol VL per 1,000 parts of dye liquor. The pH should lie in the range 3·5–4·0. Under these conditions the dye is least reactive, so that its fixation to the fibre is low, and maximum levelling and coverage of fibre irregularities can occur. Dyeing is carried out at 95°c. for 30–60 min., the longer time being required only for highly irregular yarn.

The bath is then made alkaline by adding 2·5–3·0 parts of soda ash per 1,000 parts of dye liquor. The pH of the bath should be 10–10·5. Fixation of the dye then takes place, and a further dyeing period of 60 min. at 95°c. is sufficient to develop the high wet fastness. For heavy dyeings it is advisable to complete the process by "soaping" the dyed fibre in a solution containing 2 parts of Lissapol ND and 2 parts of soda ash per 1,000 parts of water at 65°c. for 15–30 min.

For the production of dyeings of the highest standard, the dyeing temperature should be 95°c. If the temperature is reduced to 85°c. the levelling properties of the Procinyl dyes during the initial stage of dyeing will be impaired in the same way as in the case of disperse dyes. Also, the degree of fixation and washing fastness developed during the second stage of dyeing will be a little lower. Dyeing at temperatures below 80°c. results in a more marked reduction in the degree of fixation and washing fastness. However, dry-heat setting of the nylon, after dyeing, stimulates reaction between dye and fibre, and can be used to obtain the full washing fastness of dyeings which have been dyed at too low a temperature.

This general process can be used to apply Procinyl dyes to nylon fibres in most types of dyeing machinery, e.g. the winch, the paddle dyeing machine, and the jig; if the jig is used, it is best enclosed in order that a temperature as near the boil as possible may be attained. Application
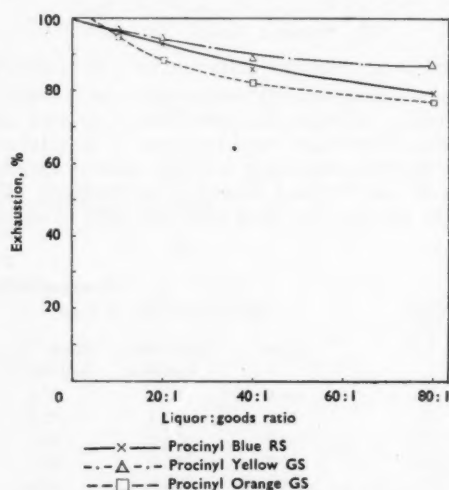

FIG. 7— Effect of Liquor:Goods Ratio on Exhaustion

to yarn packages in circulating machines has also proved quite satisfactory.

The reduction in absorption with increasing liquor ratio is more noticeable with Procinyl dyes than with conventional disperse dyes, but, as Fig. 7 shows, the effect will not be large in practice. Procinyl Orange GS is affected most, and here the exhaustion falls from 95 to 75% as the liquor ratio is increased from 10 to 50 : 1. Due allowance should therefore be made for this variation when setting the bath with dye, in order to avoid excessive shading additions.

Printing

In the printing of nylon, Procinyl dyes offer the user of disperse dyes a means of obtaining improved wet fastness properties. In general their wet fastness is of the same order as that of the best acid dyes of the level-dyeing type, e.g.—

Lissamine Fast Yellow 2G (C.I. Acid Yellow 17)
Croceine Scarlet 3B (C.I. Acid Red 73)
Solway Blue RN (C.I. Acid Blue 47)

but whereas there is a tendency for "flushing" of the outline and occasional "displacement" effects to occur when using acid dyes, Procinyl dyes, like conventional disperse dyes, are free from these defects.

The Procinyl dyes may be printed on nylon using a printing paste containing acetic acid and sodium acetate, which, during the steaming process, develops slight alkalinity, thus providing conditions for reaction to take place. The procedure is to print, dry, steam for 30 min., and soap for 5 min. at 50°C.

Fastness Properties

Examples of fastness properties of the Procinyl dyes on nylon are compared with those of disperse dyes in Table X. As would be expected, the washing and heat fastness properties of Procinyl dyes are excellent and much better than those of conventional disperse dyes, whereas the light fastness is of the same order.

A close parallel with the properties of reactive dyes on cellulose cannot be drawn. Unfixed Procion dyes are removed during washing off, and the properties of the finished dyeing are due solely to the fixed dye which remains. With Procinyl dyes, on the other hand, a proportion of unfixed dye remains on the fibre after washing off. This causes only a minor reduction in fastness to subsequent washing, because in this case the unfixed dye itself has a moderate wash fastness, and being present only as a minor constituent

has little effect on the overall fastness. A useful and unexplained property of Procinyl dyes is their high fastness to heat sublimation. This could be considered to be associated with their reaction with the fibre, were it not for the fact that on cellulose triacetate, where there is strong evidence against reaction, the heat sublimation properties are markedly superior to those of conventional dyes. On nylon the heat sublimation fastness is excellent.

6-NYLON

6-Nylon fibres such as Perlon, Enkalon, and Amilan may be dyed with Procinyl dyes by the methods already described for 6,6-nylon. The properties of the dyes on 6-nylon are very similar to those on 6,6-nylon; the rate of dyeing is higher, and the temperature-range properties are a little better.

SECONDARY CELLULOSE ACETATE AND CELLULOSE TRIACETATE

Procinyl dyes may be applied to secondary cellulose acetate and cellulose triacetate in the same way as normal disperse dyes. Although there is no evidence of reaction with these fibres, fastness to wet treatments is generally somewhat higher than with normal disperse dyes. The temperature-range properties are generally poor, however, and the Procinyl dyes are of limited interest for dyeing these fibres.

Procinyl dyes are of more interest when applied by printing; on secondary cellulose acetate they offer the advantages over conventional disperse dyes of a reduced steaming time (15 min. as against 30 min.) and superior washing fastness. When applied to cellulose triacetate by printing, their wet fastness is comparable with that of vat dyes, and their superior sublimation fastness and brightness of colour make them particularly suitable for application to pleated styles. In addition, they are simpler to apply than are vat dyes, a conventional recipe for disperse dyes being used, with the addition of urea and steaming for 30 min. For full colours it is necessary to steam at 10 lb./sq.in., however.

POLYACRYLONITRILE FIBRES

On polyacrylonitrile fibres such as Orlon and Courtelle the build-up of Procinyl dyes is limited; there is strong evidence that no reaction with the fibre occurs, and they have no advantages over disperse dyes.

However, on the modified polyacrylonitrile fibre Acrilan, the Procinyl dyes build up well and, if

TABLE X
Fastness Properties of Procinyl and Disperse Dyes on 6,6-Nylon

| Dye | Washing Fastness | | | | | | Perspiration | | | Heat Setting | | Light Fastness |
| | 1 Wash at 85°C. | | | 5 Washes at 100°C. | | | | | | | | |
	Effect on Dyeing	Staining of Nylon	Staining of Cotton	Effect on Dyeing	Staining of Nylon	Staining of Cotton	Effect on Dyeing	Staining of Nylon	Staining of Wool	Effect on Dyeing	Staining of Nylon	(Daylight)
Procinyl Yellow G	5	4–5	5	4	3	5	5	5	5	5	5	6
Procinyl Orange G	4	4–5	5	3–4	4–5	5	5	4	4	5	5	5
Procinyl Scarlet G	5	4–5	5	4	4–5	5	5	4–5	4–5	5	5	5
Procinyl Blue R	5	4–5	5	4	5	5	5	5	5	5	5	4–5 (redder)
Dispersol Fast Yellow G	3	2	4–5	–	–	–	5	3	4	4–5	5	6–7
Dispersol Fast Orange G	1	1	3	–	–	–	4	2	3	4	2	4–5
Dispersol Fast Scarlet B	2	2	4–5	–	–	–	5	3	4	4	3–4	3–4
Duranol Brilliant Blue BN	2	2	4	–	–	–	5	2	3–4	4	2	4 (redder)

applied by a method similar to that used for nylon, give dyeings of very high wet fastness. There is some evidence that the dyes react with this fibre, as might be expected in view of its basic nature. A mixture of dimethylformamide and chlorobenzene will not remove the dyes completely from the fibre, and Acrilan fibre dyed with Procinyl Blue RS is much more difficult to dissolve in dimethylformamide than is undyed Acrilan. However, most Procinyl dyes are of minor importance on Acrilan because of their poor light fastness on this fibre.

POLYESTER FIBRES

In general the Procinyl dyes are not useful for dyeing Terylene and other polyester fibres because of their unsatisfactory light fastness and uptake.

Procinyl Yellow G is an important exception, however. It possesses very good light fastness in heavy depths and outstanding fastness to heat treatment, giving faster results in the latter respect than have hitherto been possible. In spite of this excellent heat fastness, there is strong evidence that there is no chemical reaction between dye and fibre, as the dye is extracted from the fibre by organic solvents, and moreover it is applied by the normal method for conventional disperse dyes, and can be used in mixtures with selected members of the latter range.

Conclusions

The introduction of Procinyl dyes represents a further development in the field of reactive dyes for textiles. This application of the principle of reaction between dye and fibre makes it possible to combine good levelling properties with high wet fastness, by dyeing first in an acid dyebath, in which levelling takes place, and then in an alkaline dyebath, in which reaction with the fibre occurs. This process is simple, may be carried out in conventional machinery, and does not entail the use of abnormal dyeing conditions or special reagents. By the use of Procinyl dyes it is now possible to dye nylon textiles to fast, bright colours with excellent coverage of fibre irregularities.

*   *   *

The authors acknowledge their great indebtedness in preparing this paper to many colleagues in the Dyehouse and Research Departments of Imperial Chemical Industries Ltd., Dyestuffs Division, who have contributed to the development of this new range of dyes. In particular they thank Messrs. H. R. Hadfield and W. P. Mills, who have been largely responsible for the practical methods of application of Procinyl dyes, and also Dr. C. Preston for helpful discussions on the theoretical aspects of the paper.

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Discussion

Prof. E. Elöd: I should like to congratulate the lecturer and his co-workers on these new and important developments in nylon dyeing. From the theoretical point of view it might be expected, in view of the analogies in the chemical and X-ray structures between polyamide fibres and silk, that the latter fibre would also be dyed by Procinyl dyes under the same conditions. According to the lecturer, a chemical reaction takes place between the Procinyl dyes and the amino groups in the fibres. Therefore, it must be expected that, by deamination of nylon, the amount of dye absorbed should decrease according to the reduction in the content of amino groups. From the theoretical point of view of estimating the true chemical reaction between Procinyl dyes and polyamide fibres, this would undoubtedly be of interest. The "alkali shock" process used here for the fixation of Procinyl dyes shows some analogy to the "acid shock" process for dyeing wool.

Dr. Vickerstaff: As Professor Elöd suggests, the Procinyl dyes can be used for dyeing silk, but they show no advantage in dyeing properties over Procion dyes, and since the latter are generally of higher light fastness and in addition cover a much wider shade range, the Procinyl dyes are at present of little interest on this fibre. As regards deamination of nylon, this experiment would certainly be of interest, but has not so far been undertaken.

Mr. E. J. Koller: What is the reactive system in the new Procinyl dyes, and in what respect does it differ from that of the earlier Procion dyes?

Dr. Vickerstaff: The essential difference between the Procion and Procinyl dyes is that the former are water-soluble dyes containing sulphonic groups, whereas the latter are insoluble disperse dyes containing no ionisable groups. Procion dyes, therefore, behave in the first place as acid dyes and tend to accentuate any small chemical differences between different nylon fibres. In addition, the reactive group in Procion dyes is of a relatively high reactivity and will combine with amino groups in nylon under both acid and alkaline conditions. It is, therefore, impossible to apply Procion dyes under any conditions which prevent chemical reaction, so that little or no levelling can take place. In consequence, any physical differences between fibres which allow these dyes to penetrate more or less easily are shown up in the initial dyeing stages and cannot be eliminated by the levelling treatment. In searching for suitable dyes for nylon, it was necessary to employ a much less reactive group. In the first place the dyeing of nylon must

be carried out at temperatures near 100°c. in order to speed up the diffusion process into this compact fibre and so shorten the dyeing time to a reasonable length. Because of this increase in temperature a reactive grouping of much lower activity is required, as compared with the Procion dyes which are applied to cellulose in the cold. In the second place a less reactive grouping is required in order that the reactivity may be controlled by pH. In the chosen system, the reactivity is so low that no significant reaction takes place at temperatures around 100°c. at a pH below 4. The chemical nature of the reactive group cannot be disclosed at this stage, but it does contain a chlorine atom which combines with the amino groups in the nylon.

Mr. J. T. MARSH: Is there any likelihood of the recent methods of making polyamides by interfacial condensation giving a product which will be easier to dye?

Dr. VICKERSTAFF: It is difficult to say at this stage whether fibres produced in this way will be more consistent and reproducible in their chemical constitution than fibres produced by bulk reaction followed by melt spinning. However, it is unlikely that the difference will disappear entirely. The physical differences between fibres arise mainly in the drawing stage, due to the difficulty of controlling this process with 100% accuracy, and since a drawing process will almost certainly be involved, even with new methods of making polyamides, it is probable that this source of irregularity will remain; the chemical differences between fibres are essentially differences of molecular weight. Presumably fibres made by this new process will also have a definite molecular weight, and I should expect small differences in molecular weight to arise, which will result in slightly different amino end-group contents, so that chemical differences may also persist.

Dr. H. ZOLLINGER: A graduate student in the Institute of Dye Chemistry, University of Basle, who is investigating adsorption isotherms of disperse dyes on polyamides, has studied the fixation of Procinyl-like reactive dyes and their hydrolysed products. We have been able to show that the hydrolysed dye has a considerable affinity for 6,6-nylon in an acidic medium, but practically no affinity in an alkaline dyebath. We think that this explains the contrast with respect to degree of fixation of reactive dyes on nylon and cellulosic fibres, respectively. Hydrolysed reactive dyes for cellulose have a considerable affinity for the substrate, whereas hydrolysed Procinyl dyes have no affinity for nylon under dyebath conditions, i.e. at pH > 8.

Dr. VICKERSTAFF: The results described by Dr. Zollinger are completely at variance with our own observations. It is not clear whether Dr. Zollinger has in fact investigated the Procinyl dyes, or merely some compounds of a reactive type which are considered to be similar in behaviour. With Procinyl dyes, the hydrolysed product has a high affinity for nylon, although admittedly this is lower in an alkaline solution than in acid solution. The high affinity is revealed by the fact that it is difficult to remove the hydrolysed dye by washing,

so that an estimate of the chemically combined dye can finally be obtained by extracting the hydrolysed dye with propanol. I am surprised to hear that Dr. Zollinger considers that hydrolysed reactive dyes of the Procion type have a considerable affinity for cellulose. As a result of our own experiments, we consider the affinity of these dyes for cellulose in absence of electrolyte, is very low indeed. It is obvious that a further comparison of Dr. Zollinger's results with our own will be necessary in order to resolve this matter.

Prof. R. H. PETERS: The authors have brought strong evidence to show that combination of dye with the fibre occurs. However, combination with the hydrogen atom of the amide group usually requires rather stringent conditions, so I should like to ask the following questions—

(a) Is it possible that the dye may combine with itself to form dimers or trimers, or even polymers in the fibre? These may not be leached out easily with propanol.

(b) The model compound mentioned (p. 106) is a substituted urea (as well as being an amide). May not the dye have combined with the urea portion rather than the amide group?

(c) The combination of the dye with the primary amine end-group may produce a compound with the properties of a secondary amine (constitution of the dye being unknown); if this is so, could this then react with a second molecule of dye? This would make the possible uptake of dye equal to twice that of the amine end-content.

Dr. VICKERSTAFF: In reply to the first question, certain of the Procinyl dyes might conceivably react with themselves, and this possibility was carefully considered. It was for this reason that the experiment was carried out whereby dyed nylon fibre was dissolved in o-chlorophenol and the nylon precipitated by propanol. Under these conditions any mechanical retention of dye by the fibre is eliminated, and we consider that this possibility may be ignored. Furthermore, certain of the dyes are not capable of reaction with themselves.

It is possible that the dye may have reacted with the urea portion of the first compound, but evidence of reaction was also obtained with dibenzoylhexamethylenediamine.

The possibility that two molecules of dye may react with the amino end-groups in nylon has not so far been examined and cannot be eliminated as a possibility from the results of the experiments to date.

Dr. J. WEGMANN: Since about 10–20% of the Procinyl dye remains in the fibre in an inactivated state, but without affecting the fastness properties, the question arises as to whether it is necessary for the Procinyl dye to react with the fibre at all.

Dr. VICKERSTAFF: It is true that the uncombined reactive dye appears to have a high affinity for nylon and has relatively high wet fastness

properties. Nevertheless, if conditions in processing are such as to give incomplete reaction, then a deterioration in wet fastness properties can be observed. In such cases, however, it is possible to improve the wet fastness properties by a further alkaline heat-treatment, which suggests that the uncombined dye in the original dyeing is still capable of reaction.

CORRESPONDENCE

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Vapour-phase Dyeing with Disperse Dyes

The investigations of Majury[1] on the system solid dye–dye vapour–substrate have been extended by us, with emphasis on the kinetic aspects. Majury has studied the rate of absorption of unsaturated *p*-nitroaniline vapour by secondary cellulose acetate. We have calculated from Majury's results that the diffusion coefficient of this substance, for a temperature of 150°c. and a relative vapour pressure of 0·063, is $1·3 \times 10^{-10}$ cm.²/sec. approx.

Apparent diffusion coefficients for larger molecules, including some disperse dyes, may be calculated from our measurements on the rate of absorption of saturated vapour by secondary acetate. The rate was measured by suspending a

anhydrous diffusion since, according to Barrer[6], fluctuation in thermal energy would ensure the presence of a number of "holes" sufficient for diffusion to occur.

We have also shown, in experiments similar to those of Jensen[7], that an apparent second-order transition temperature of 125°c. in cellulose acetate film is lowered to 117°c. in the presence of the saturated vapour of 1-methylaminoanthraquinone. The shrinkage temperature is also lowered from 184° to 174°c., indicating that the dye may be acting as a plasticiser at high temperatures. Such action probably accounts for the high saturation values obtained in vapour-phase dyeing. The dyed films remain transparent, but on standing

TABLE I

Dye	Temperature (°c.)	Saturation Value (g./100 g. dry cellulose acetate)	Diffusion Coefficient D (cm.²/sec. $\times 10^{13}$)
Azobenzene	100	14·19	5·05
p-Aminoazobenzene	100	32·29	1·59
NN-Dimethyl-*p*-aminoazobenzene	133	10·08	8·42
1-Methylaminoanthraquinone	150	9·54	22·03
1-*β*-Hydroxyethylaminoanthraquinone	150	10·80	0·853

known amount of anhydrous film from a previously calibrated helical spring of silica in an evacuated glass envelope containing solid dye. The envelope was totally enclosed in a metal-block thermostat and the deflection of the spring was observed through a mica window of 1 cm. diameter by means of a cathetometer.

The results (Table I) are not complete and it is hoped to submit more complete results later. The values of D have been calculated from the equation used by McBain[2] for non-steady-state diffusion and refer to a total concentration of 0·75 g. dye per 100 g. anhydrous acetate. Owing to the small rate of absorption from the vapour phase, especially of the larger dye molecules, it has not yet been possible to obtain sufficient results to compare the activation energies of vapour-phase diffusion with those obtained by conventional dyeing.

These values of D are very much smaller than those obtained from experiments on the rate of dyeing using aqueous dyebaths[3-5], possibly owing to the unswollen state of the anhydrous cellulose acetate film. It may not be necessary to postulate the existence of gross pores and capillaries in

for several weeks under atmospheric conditions develop a surface layer of needle-like dye crystals which are easily visible under the microscope. This phenomenon has previously been observed[8] in the migration of dyes in cellulose acetate mouldings, but not so far as is known in film dyed from the vapour.

C. L. BIRD AND F. JONES
R. S. BRADLEY

DEPARTMENT OF COLOUR CHEMISTRY AND DYEING
DEPARTMENT OF INORGANIC AND STRUCTURAL CHEMISTRY
THE UNIVERSITY
LEEDS 2

15th December 1959

[1] Majury, J.S.D.C., **72**, 41 (1956).
[2] McBain, *Z. phys. Chem.*, **68**, 471 (1909); cf. also Vickerstaff, *The Physical Chemistry of Dyeing* (London: Oliver & Boyd. 2nd edition 1954), pp. 130 ff.
[3] Majury, J.S.D.C., **70**, 445 (1954).
[4] Ghionis, *Dr. rer. nat. Thesis* (Technische Hochschule, Stuttgart 1958).
[5] Bird, Manchester, and Scott, J.S.D.C., **72**, 49 (1956).
[6] Barrer, *Trans. Faraday Soc.*, **35**, 644 (1939).
[7] Jensen, *J. Polymer Sci.*, **28**, 635 (1958).
[8] Deverell-Smith, *Hexagon Digest*, **15**, 3 (1953).

Notes

Election of a Fellow

At the meeting of Council held on 6th January 1960 the following election was made—

Walter Percival Mills

Blackley, Manchester; Assistant Technical Officer, Dyehouse Department, Imperial Chemical Industries Ltd.

Election of Associates

At the meeting of Council held on 15th July 1959 the following elections were made—

Brian Acton

Cheadle, Cheshire; Instructor, The Manchester College of Science and Technology

Margaret Brooks

Whitefield, Manchester; Technical Assistant, The Geigy Co. Ltd., Rhodes

Harry Bush

Leeds; Lecturer, Arie Schenkar School, Ramat Gan, Israel

Michael Dunsmore

Otley, Yorkshire; Technical Dyer, The Bradford Dyers' Association Ltd.

Robert D. Ellor

Woodley, near Stockport, Cheshire; Laboratory Assistant, Courtaulds Ltd., Droylsden

Ian Fleming

Glasgow; Textile Apprentice, J. & P. Coats Ltd., Paisley, Scotland

Leonard Hughes

Denton, Manchester; Dyer, R. P. Lawson & Son Ltd., Manchester

Derek Hunt

Blackley, Manchester; Assistant Technical Officer, Imperial Chemical Industries Ltd., Dyestuffs Division

Brajendra K. Kumar

Bombay, India; Dyeing Master, Castle Mills, Bombay

Roderick McDonald

Paisley, Scotland; Research Assistant, J. & P. Coats Ltd., Paisley, Scotland

Janusz Zdan-Michajlowicz

Sherwood, Nottingham; Chemist, W. E. Saxby Ltd., Nottingham

Geoffrey Mizon

Huddersfield, Yorkshire; Assistant Dyer, John Brooke & Sons Ltd., Huddersfield

Thomas A. Nutton

Denton, Manchester; Colourist, Courtaulds Ltd., Droylsden

Bernard J. O'Hare

Romiley, Stockport, Cheshire; Chemist, The Geigy Co. Ltd., Rhodes, Manchester

Jack Sharp

Burley-in-Wharfedale, Yorkshire; Laboratory Assistant, Fibres Division,
Imperial Chemical Industries Ltd., Harrogate

Christopher C. Wallis

Baguley, Manchester; Technical Sales Representative, B.I.P. Chemicals Ltd., Manchester

Kenneth D. Wilson

Bradford, Yorkshire; Apprentice Technical Dyer, The Bradford Dyers' Association Ltd.

Parliamentary and Scientific Committee Conversazione

The Society took part on 9th December 1959 in a Conversazione at the Royal Society's premises in Burlington House, London. The Conversazione was arranged by the Parliamentary and Scientific Committee and took the form of an exhibition whose theme was "Science in Everyday Life". The Society's exhibit was mainly devoted to Colour Fastness and consisted of an illuminated panel $4\frac{1}{2}' \times 3'$ showing the scope of the Society's testing methods and their relation to the British Standards Institution and the International Organisation for Standardisation. Light and washing fastness testing were illustrated in detail and a full scale transparent model of an oscillatory dyeing machine adapted for wash-fastness testing was operating. The new *Colour Index* and other publications of the Society were also prominently displayed.

The guests, who included Mr. Clement Davies, Viscount and Lady Hailsham, and Viscount Samuel, were received by Lord Morrison of Lambeth, President of the Parliamentary and Scientific Committee, and Sir Cyril Hinshelwood, President of the Royal Society.

Liaison between British and Indian Research Workers

Dr. H. R. Ambler, O.B.E., F.R.I.C., has been appointed to the newly created post of Scientific Adviser to the U.K. High Commissioner in New Delhi. Among his duties will be the furthering of exchange of information between British and Indian research workers.

Manufacture of Dyes in India— Its Effect on Imports

As a result of the growth of the manufacture of dyes in India import of dyes into that country has dropped from Rs. 150 million (£11,250,000) to Rs. 120 million (£9,000,000). There has been complete cessation of imports of Sulphur Black, azoic compositions and most azoic diazo and coupling components, Jade Green and blue vat dyes, and Methylene Blue.

Oil and Colour Chemists' Association Twelfth Technical Exhibition 1960

The official guide to this exhibition which will be held on 15th, 16th and 17th March 1960 is available free of charge on application to the General Secretary of the Oil and Colour Chemists' Association, Wax Chandlers' Hall, Gresham Street. London E.C.2.

Biennial Conference

This will take place in Torquay, Devon, from 30th May to 3rd June 1961 under the provisional title "The Physical Chemistry of Surface Coatings". Those wishing to have details should write to the General Secretary of the Association, at the address given above, to ensure that they will be sent to them at the same time at the end of 1960 as they are despatched to members of the Association.

1960 Dornbirn Fair, Austria

At this fair to be held from 7–14th August 1960 it is anticipated there will be about 1000 exhibitors including many British manufacturers of textiles, dyes and chemicals, and textile machinery.

There will be a special display of the products of the Vorarlberg, Austria's textile province, which display will include both home and factory produced textiles and textile machinery.

Meetings of Council and Committees January 1960

Council— 6th
Examinations Board— 6th
Dyeing Properties of Disperse Dyes— 13th
Publications— 19th
Diplomas— 20th
Finance and General Purposes— 22th
International Relations Committee— 27th

New Books and Publications

Annual Reports on the Progress of Chemistry for 1958
Volume 45

London: The Chemical Society. 1959. Pp. 527. Price, 40s. 0d.

These ever welcome annual summaries deal with their subject matter in the five main sections of General and Physical, Inorganic, Organic, Biological, and Analytical Chemistry, together with the biennial survey of Crystallography.

Under *General and Physical Chemistry*, the report concerns separate and limited topics, so that this year's coverage is of a more specialised character, but although incomplete in some directions, it is intended to consider eventually all the important physico-chemical subjects over a period of two or three years. The publications now surveyed are on: ion association and acid-base equilibria in ionic solutions and electrode processes, particular attention being given to adsorption problems; transformations occurring in organic molecules and radicals; intermolecular energy transfers in both liquid and gaseous systems; and polymerisations induced by radicals. An account is also included of the attempts to determine the precise shapes and force fields of relatively simple molecules.

The report on *Inorganic Chemistry* follows previous patterns, viz. systematic treatment of the elements according to the long form of the Periodic Table. Also serious consideration has been given to choice of a unified scale for atomic

weights to replace the two oxygen scales, and are based on the exact number12 as the assigned mass of carbon-12 appears to offer the best promise of acceptance. Of unusual interest is the development of a theory for the aromatic character of cyclic phosphoronitrile chlorides $(PNCl_2)_n$, wherein both the trimeric and tetrameric rings (containing 6 and 8 electrons respectively) are aromatic, in contrast to benzene and cyclo-octatetrene for which only the six-membered ring is aromatic. Mention is made of recent reviews on "stereochemistry of inorganic molecules and complex ions", "high-temperature chemistry", "polarography in non-aqueous solutions", "ortho-salts and maximum oxygen co-ordination", "inorganic high polymers", and "vibrational spectroscopy and its application in structural inorganic chemistry".

Organic Chemistry still remains by far the largest section. It is noted how use of high-speed computers has facilitated the complex calculations necessary for application of quantum mechanics to complex structures, e.g. the colour to be expected of an hitherto unknown hydrocarbon. The great activity in study of the spectroscopic and other properties of carbonium ions (over 350 papers during the past two years) is recorded, also use of kinetic isotope effects for elucidating the nature of the rate- and product-controlling steps of chemical reactions. Reference is made to an important series of papers dealing with the mechanisms of nitrosation by the nitrosonium ion and its carriers, and to formation of arylpentazoles by reaction of aromatic diazonium chlorides with lithium azide. Nuclear and proton magnetic resonance spectroscopy continue to have many applications, and among them is locating the substituents in furan rings and in *N*-heteroaromatic systems, and determination of the ring fusion of decalins. A new hetero-cyclic aromatic system, containing the $-\overset{+}{N}H\colon\overset{-}{B}H-$ groups in positions 9,10 of phenanthrene, is mentioned. Developments in the chemistry of polysaccharides receive attention. Much work has been recorded on the mechanism of diazotisation of primary aromatic amines, which is regarded as an *N*-nitrosation, and, in absence of neucleophilic anions (other than nitrite), the available agents are the nitrous acidium ion, $^+H_2NO_2$, and dinitrogen trioxide, N_2O_3. The slow conversion of a diazonium ion into the *anti*-diazotate has been studied, and existence of both the *syn*-diazotate and the conjugate acid of the *anti*-diazotate demonstrated. Trapping of otherwise short-lived free radicals in solids at low temperatures continues to excite interest, while several new aliphatic azo-compounds are used as sources of free radicals. Phenyl radicals are shown to occur during the thermal decomposition of diazoaminobenzene and to react with aromatic substrates in the expected manner. An outstanding preparation is that of the stable triphenylmethyl free radical (1) which is considered to have a planar configuration as a result of the two ether bridges, and is stable despite their steric restraint. The heterocyclic triphenylmethyl anologue, 2-methyl-tetrazol-5-yldiphenyl methyl (2), is also stable.
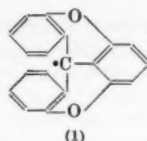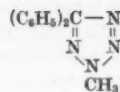
Analytical Chemistry is treated mainly as in previous reports. Interest in gas–liquid and gas–solid chromatography is at a high level, emphasis being on more sensitive means of detection of separated fractions. In polarography, alternate electrodes to the conventional dropping mercury one are proposed. Non-aqueous titrimetry and flame photometry are becoming increasingly important, and the possibilities of toluene-3,4-dithiol as an analytical reagent in place of hydrogen sulphide are beginning to be realised. Finally, analysts in many fields are finding useful the flask combustion method of preliminary combustion in oxygen.

Crystallography is the concluding theme, and since over 750 publications have appeared during the past two years, the coverage is necessarily incomplete with a bias in favour of molecular-structure analysis. An outstanding discovery is that in the crystal of β-naphthol there are two sets of non-equivalent molecules.

Since the report contains over 4000 references involving over 5000 names, its unique value for chemists everywhere is self-evident.

H. H. HODGSON

Techniques of Polymer Characterisation

Edited by P. W. Allen. London and New York: Butterworths Scientific Publications and Academic Press Inc. 1959. Pp. xiv + 256. Price, 50s. 0d. ($9.50).

Although there are a number of textbooks which provide a detailed theoretical background to fractionation, molecular weight determination and other methods of characterising high polymers, few, if any, give adequate details of the techniques employed. Such details are often unpublished or not readily accessible. As a result, newcomers to the field find it difficult to obtain the essential practical knowledge and acquire the necessary techniques. This book, the work of a team of experts in particular fields of polymer characterisation, is designed to fill the gap.

Methods of polymer characterisation generally involve the use of dilute solutions. P. W. Allen, the editor of the book, provides an introductory chapter which includes valuable information on the preparation and handling of these. A chapter on "Fractionation" is contributed by R. W. Hall. H. J. Hookway writes on "Osmotic Determination of Molecular Weights" and D. F. Rushman on other methods of determining number-average molecular weights by physical methods. A chapter on "Light Scattering Techniques" is contributed by F. W. Peaker and one on "Viscometry" by P. F. Onyon. G. F. Price is the author of an account of "Techniques of End-group Analysis" and a final, topical chapter on "Characterisation of Block and Graft Copolymers" is contributed by R. J. Ceresa. Each chapter consists of a brief theoretical introduction,

a detailed description of the methods and apparatus used and a concluding section on interpretation of results. Detailed development and derivation of the formulae involved are not given, it being assumed that the reader has studied these previously.

In such a book as this it is essential that different methods should be critically assessed, their scope and limitations clearly shown, descriptions of apparatus and techniques sufficiently detailed and adequate references provided. These requirements are generally well met. The extensive and accurate bibliography is a particularly valuable feature. The sections dealing with interpretation of results might be extended, perhaps with reference to results obtained with particular polymers and the interpretation of apparently anomalous results such as those which may result from association of polymer.

The book is primarily intended for the post-graduate research worker concerned with fundamental research. The chapter on characterisation of block and graft copolymers is perhaps of more general interest. That dealing with techniques of end-group analysis will probably be of most interest to readers of this *Journal*. Teachers of polymer chemistry will find the book of great help in designing practical work. The descriptions of apparatus and methods are clear and concise and there are many clear diagrams illustrating apparatus. As Professor Gee points out in the preface, few books are likely to be of such direct and practical utility to practitioners of the subject. For a book of this type the price is very reasonable.

W. R. MOORE

Shrinkage
A Survey of Shrinkage Problems and their Solutions with special reference to Industrial Overalls
Overall Manufacturers' Association of Great Britain. 1959. Pp. 42. Price, 5s. 0d.

For two years a working party made of members from all interested bodies has been engaged in making detailed inquiries in problems relating to cloth, making-up, laundering, and home washing. The results of these inquiries are set out in this booklet, which should be of interest to all concerned in the manufacture of cotton cloths for industrial overalls, and to the makers of such clothing and those who have to undertake their cleaning after use.

C. O. CLARK

High Temperature Laundering of Woollen Hospital Blankets
By J. C. Dickinson, R. E. Wagg, and G. D. Fairchild. International Wool Secretariat: London, June 1959. Pp. 25. Free on application.

This is a joint report prepared by the British Launderers' Research Association and the International Wool Secretariat. It describes work which indicates that suitable types of wool blankets, especially those which have received an adequate shrink resist treatment, will last a reasonable time even if laundered repeatedly at a temperature high enough to kill vegetative bacteria rapidly.

C. O. CLARK

Filmdruck
Rapport, Farbauszüge, Schablonen
By R. Künzl. Stuttgart: Konradin-Verlag Robert Kohlhammer, GmbH. 1959. Textheft, pp. 84, Bildheft, pp. 75. Price, DM 18.90.

The work, in its present conception, is divided into 2 volumes. The first (84 pp.) contains the text dealing with repeats, colour-draughts, and screens. The second part (76 pp.) is supplementary and illustrates with sketches, photographs etc. the subjects dealt with in Part I, so making understanding of it very easy.

The first 24 pages of Part I deal with the production of suitable printing designs. Starting from elementary rules, such as how to construct a right angle, Künzl soon approaches the main issue dealing with the various possibilities of producing repeats that do not contort the final sketch. Practical advice is also given on the multiplication, enlarging, and reduction of designs and repeats, whereby the modern photographic method is referred to on its full merits. This part of the publication is of main interest for the designer and deserves careful study by students who intend to take up textile designing. This does not mean that many a textile designer established in the trade could not gather some valuable hints from these pages, which might save the printer the frequent need for a purchased design having to be re-drawn before it is fit to be transferred to the screens.

Pp. 25 to 65 are concerned with methods of bringing a design into the required form to be transferable to the screens. Four ways are indicated of preparing the colour-draughts, which can be done either by hand-painting or by cutting into a red lacquer-coated film, as well as by two different photographic methods.

A separate chapter deals in detail with the mounting of the colour-draughts. The information provided in these pages should be of great interest to the vast majority of screen makers, who have adopted the photo-chemical method of production.

The last chapter deals with the actual making of the screens. Advice is given about the various qualities of gauze on the market and methods of fixing it to the frame. This is followed by a description of various photo-chemical methods of screen making written in a very clear manner and in conclusion the Japanese wax-paper-method is discussed.

An index of suppliers of the various proprietary materials mentioned in the book makes it the more valuable.

W. TAUSSIG

Rapportrichtiges Musterzeichnen
By R. Künzl. Stuttgart: Konradin-Verlag Robert Kohlhammer, GmbH. 1959. Pp. 56. Price, DM 8.50.

This is a reprint of the first chapter of Part I of the work dealt with in the preceding review together with the relevant illustrations from Part II. It is a good idea to bring out a self-contained extract for the textile designer, who is not interested in the actual making of the screen.

W. TAUSSIG

Fiber to Fabric
3rd Edition

By M. D. Potter and B. P. Corbman. McGraw-Hill Book Co. Inc.; New York, 1959. Pp. 342. Price, 33s. 0d.

This edition retains the plan of the former edition (J.S.D.C., **72** (1956) 58) with some refinements such as inclusion of a separate chapter devoted to knitting, an account of new and improved methods of finishing, e.g. wash-and-wear finishes, descriptions of the new fibres and their blends etc. It is well suited as a textbook for the reading of elementary textile technology.

C. O. CLARK

Library of the Academy of Sciences of the U.S.S.R. Guide Book

By I. F. Grigor'eva, T. M. Koval'chuk, and T. I. Skripkina. Moscow and Leningrad: Academy of Sciences of the U.S.S.R. Press. 1959. Pp. 112 + frontispiece and 8 plates.

A guide for users of the library with information relating to the research libraries of academic institutions in Leningrad. Particulars are given of exhibits and tours of the library likely to be of interest to visitors.

C. O. CLARK

International Conference on Co-ordination Chemistry. London 1959

Special Publication, No. 13. London: Chemical Society. 1959. Pp. iii + 204. Price, 42s. 0d. ($6.00).

This slim volume is a report on a conference which was held in London in April 1959 and as such it reflects the trend of current thought in co-ordination chemistry. The main part of the book consists of addresses by seven international authorities but in addition there are abstracts of papers by researchers in many diverse fields, some of whom are not less distinguished than the principal contributors. Opinion will vary as to the relative importance of the addresses but to the reviewer K. Ziegler's "New Aspects of Some Organometallic Compounds", H. W. Steinberg and I. Wender's "Metal Carbonyls and Related Compounds as Catalytic Intermediates in Organic Syntheses", E. O. Fischer's "Co-ordination Compounds of Unsaturated Hydrocarbons with Metals", L. E. Orgel's "Metal–Ligand Bonds", and R. Nast's "Complex Acetylides of Transition Metals" are

outstanding in scope and penetration. Ziegler's address is concerned mainly with the basic chemistry and uses of aluminium alkyls, Steinberg and Wender review a host of carbonylation reactions which emerged from a study of the Fischer–Tropsch reaction but soon deployed over a wide field of preparative chemistry, E. O. Fischer contributes a most comprehensive address beginning with the electronic structures of metal–carbon bonds and advancing through a wealth of examples to a detailed and fundamental structural study of metal–carbon compounds. R. Nast contributes a somewhat similar address on a different aspect of the subject, but again wide in scope and fundamental in treatment. L. Orgel's address, as one would expect, is concerned with basic theory mainly in relation to the reaction of iron carbonyls with acetylenes.

The abstracts of other papers presented at the conference are necessarily brief and for this reason although they do not lack merit their impact on the reader is more slight. They are concerned with a very wide variety of co-ordination compounds containing Al, Ti, Cr, Mn, Pt, Co, Ni, Fe, Ir, Rh, Ag, Cd, Pd, As, Cu, Hg, Mo, W, Re, Zr, Nb, Ta, B, Ru, Li, Si, In, Os, Va, Na and some general questions such as light absorption of complexes, polarisation of ligands, magnetic behaviour and the kinetics of formation of some charge–transfer complexes. The following topics may be mentioned as having unusual interest: the structure of dibenzenechromium (p. 123), co-ordination compounds of aromatic hydrocarbons with silver perchlorate (p. 125), volatile copper perchlorate (p. 162), photo-induced isotopic exchange reactions of complexions (p. 164), the rôle of dye-complexes in photochemical reactions in solution and at interfaces (p. 166), the use of complexes in medicine to overcome the toxicity of radio-elements (p. 180).

Two abstracts with a direct bearing on dyestuffs are concerned with the composition and stability of metal chelates of ammonium aurintricarboxylate (p. 183) and the spectra of Fe(11) complexes of 1-nitroso-2-naphthol-3,6-disulphonic acid (p. 192).

The volume will be welcomed by libraries and specialists working with co-ordination compounds. It is not a textbook for students but a few of the principal addresses would be useful medicine for almost any chemist.

There are indexes of authors and subjects.

W. BRADLEY

Manufacturers' Publications and Pattern Cards

American Cyanamid Co.

DYES TECHNICAL BULLETIN No. 856— Microscopical Studies with the High-temperature (Pressurised) Micro-dyeoscope— This issue is a reprint of the account by Dr. H. E. Millson of the design, construction and use of the pressurised version of the original Dyeoscope and the results he obtained with it in his studies of the dyeing of a range of fibres > 100°c.

Badische Anilin- und Soda-Fabrik A.G.

PALANIL DYESTUFFS ON POLYESTER YARN— This card contains dyeings in two depths on Trevira staple fibre yarn of 32 Palanil disperse dyes, a range particularly recommended for polyester fibres. A further sixty mixture dyeings are also included and all the dyeings have been produced at 125°c. It is interesting to note that the fastness data include a very wide range of assessments of

thermal stability including contact heat (ironing for 10 sec. at 150°c. and 200°c.), hot air (1 hr. and 5 hr. at 120°c., 30 sec. at 180°c. and 200°c) and steam (decatising "a" and "b", 15 min. at 7 lb./sq.in. and 21 lb./sq.in.).

Ciba Ltd.

CIBACET DIAZO BLACK GWS— This disperse dye gives bluish blacks on secondary cellulose acetate and triacetate when diazotised and developed on the fibre with β-hydroxynaphthoic acid and is recommended for application to these fibres at all stages of processing, since as a member of the new Micro Disperse range it gives an extremely fine aqueous dispersion. On secondary cellulose acetate it may be applied by a "two-step" method, as well as by the normal three-stage method, dye and coupling component being applied in sequence in the same bath and diazotisation and coupling carried out simultaneously in a second stage. It may be applied to polyamide fibres but is less productive and gives dyeings of only moderate fastness to light. Fastness ratings on secondary cellulose acetate include— Light (daylight) (bright fibre) 4–5, hot pressing SNV 5, washing SNV a 5.

CIBACRON BRILLIANT RED B— This reactive dye gives brilliant reds on cellulosic materials. It may be applied, alone and in mixtures, by both pad–fixation and batch-wise exhaustion methods to give dyeings of the same high order of fastness obtainable using other members of the range. The card contains dyeings on cloth and yarn produced by a variety of methods and 6 mixture dyeings on continuous filament viscose rayon and mercerised cotton cloth produced by the pad–thermo fixation method.

CIBACRON BRILLIANT RED B— This card describes use of this reactive dye in printing cellulosic fibres. It may be direct printed alongside vat, solubilised vat, direct, Cibaneutrene and Oremasin dyes and on naphthol pre-pares. It is also suitable for fast coloured resists under aniline black, naphthol blue, and solubilised vat dyes. Pad-dyeings are also suitable for white and coloured resists.

COPRANTINE NAVY BLUE RLL— This direct dye gives reddish navies on cellulosic fibres when aftertreated with either copper sulphate, Coprantine Salt II or Coprantex B. It is suitable for high-temperature dyeing and for use on materials to be resin treated. Dyeings are dischargeable to white by the Coprantine discharge method. It is particularly recommended for knitted materials, furnishings, raincoat cloths, and sewing yarns and is of interest in combination with Cloth Fast Blues for navies on wool/cellulosic fibre mixtures. Fastness figures for a dyeing on cotton aftertreated with copper sulphate/acetic acid include— Light (daylight SNV) 6, washing SNV b 4, perspiration SNV 4.

COPRANTINE RED 2BLL: COPRANTINE RED GRLL— These are after-copperable direct dyes. Red 2BLL gives the brightest and bluest reds obtainable with the Coprantine range, the GRLL brand giving reds inter-mediate in hue between those obtained with Red 2G and Red RLL. Both are level dyeing and cover dead cotton. They are suitable for materials to be resin treated. Red 2BLL gives solid dyeings on cotton/viscose rayon mixtures, reserves secondary cellulose acetate rayon in pale to medium depths and is dischargeable to white with the Coprantine discharge. Fastness figures for a dyeing aftertreated with copper sulphate and acetic acid include—

	Light (Daylight, SNV)	Washing (SNV b)
Coprantine Red 2BLL	6	3–4
Coprantine Red GRLL	6	4

PAPER FAST BLACK BG–LA— The Paper Fast dyes are aqueous dispersions of pigments for colouring paper in the beater. The very small particle size ensures uniform coloration. Black BG–LA gives bluer blacks and is more productive than the older Black BN–LA. It is suitable for coloring all types of paper, including paper laminates, giving colours of very good fastness to acids and alkalis and outstanding fastness to light.

UVITEX PRS— This fluorescent brightening agent is designed for application to paper and gives a reddish white on bleached pulp, for which it has high affinity. When applied in the beater the concentration normally required is 0·02–0·08% and a very intense white is obtained by using 0·2% or more. It may also be applied in coating mixtures and in the size press. It shows good stability to alkali and acid.

CIBA REVIEW No. 133— This issue is largely devoted to Coptic textiles. Technical articles include information on Univadine W, a levelling agent for wool, Cibacron and Chlorantine Fast dyes on wool/cellulose fibre mixtures, Cibacrons and Cibacrolans for dyeing fur hat felts, and Cibacrons in wool and silk printing.

CIBACRON AND CIBACROLAN DYES ON WOOL— This card describes the application of eight Cibacron and two Cibacrolan dyes to loose wool, yarn, and cloth. Ten mixture dyeings on cloth are included to indicate the range of colours obtainable. Full details of the special Neovadine dyeing method are given. A new auxiliary product, Disperser CC, is recommended for improving levelness and penetration when using up to 2% of dye. Addition to the exhausted dyebath of up to 4% of ammonia (25%) or an amount of hexamethylene tetramine equal to half the active acid (45%) used in dyeing is advised to promote rediffusion into the dyebath of as much as possible of the unreacted dye. The Cibacron and Cibacrolan dyes are recommended primarily for deep, bright colours but not for greys, light browns, and khakis for which other ranges of wool dyes, e.g. the neutral-dyeing and acid-dyeing metal-complex types, are preferred.

Ciba Clayton Ltd.

CIBACET DYES ON CELLULOSE TRIACETATE— This card contains dyeings on cellulose triacetate cloth of thirty-six disperse dyes, one of which, Cibacet Diazo Black HD, has been diazotised and coupled with β-hydroxynaphthoic acid using a modified azoic technique in which the dye and coupling component are applied consecutively and development carried out in a fresh bath containing nitrite and acid.

CIBACRON DYES: WHITE DISCHARGE PRINTS— This card contains twenty discharges on mercerised cotton sateen pad-dyed with combinations of Cibacron dyes by the thermofix process and discharged with alkaline sodium sulphoxylate formaldehyde in presence of Discharge Salt Ciba W and zinc oxide.

Farbenfabriken Bayer AG.

DYEINGS ON UPHOLSTERY FABRICS AND PLUSH GOODS— This card contains dyeings on a wool pile/cotton back material of twenty-five fast-to-light direct cotton dyes showing the distribution of the direct dye between the two fibres and of the same dyes plus selected acid dyes to give solid dyeings, when applied by the recommended single-bath method at pH 4–5. It is claimed that this method enables dyeings to be readily reproduced since the addition of Mesitol WL and Avolan AL ensures that staining of the wool by the direct dye is reduced to a minimum. Further, since dyeing is carried out under acid conditions, and is not prolonged, the quality of the wool pile is unimpaired. The scope of the method is illustrated by 20 solid mixture dyeings on a typical plush fabric and a further 16 two-colour dyeings on an uncut wool pile/cotton back material. The resisting and levelling action of the two auxiliary products is such that shading of both the wool and cellulosic components can be safely carried out.

PADDED DYEINGS WITH INDANTHREN DYESTUFFS— This card contains dyeings in five depths, on cotton cloth, of thirty-six Indanthren vat dyes applied by the pigmentation –jig development method. In addition there are forty-one mixture dyeings in two depths and a further sixty-four single depth mixture dyeings of typical colours for shirtings and gabardine cloths.

INDANTHREN DYESTUFFS— This card describes thirty-four Indanthren vat dyes each of which is shown dyed in three depths on no less than six types of yarn, cotton, mercerised cotton, viscose rayon (cont. filament and spun staple) and cuprammonium rayon (cont. filament and spun staple). The fastness data appended alongside the dyeings and the information given in the text (58 pp.) is equally comprehensive.

ISOLAN DYES ON COMBED MATERIAL— This card contains dyeings in three depths on slubbing of 20 Isolan 2:1 dye:metal complex dyes and 5 Isonal fast-to-milling acid dyes for use in conjunction with them to provide

brightness where required. The Isonal dyes are, in fact, selected established dyes, as is indicated by the old name which is given alongside the new one. They are recommended for application in presence of ammonium acetate at pH 5·5 approx. Dyeings in three depths of a very comprehensive range of seventy mixtures are also included.

ISOLAN DYES ON KNITTING YARN— This card contains eighty dyeings on yarns of mixtures of Isolan metal-complex dyes and fast-to-milling acid dyes (the group now known as the Isonal dyes).

DYEING OF ISOLAN DYESTUFFS ON WOOLLEN GABARDINE— This card contains fifty-four dyeings on wool gabardine of mixtures of Isolan metal-complex dyes and the group fast-to-milling acid dyes (now known as the Isonal dyes).

SIRIUS SUPRA BORDEAUX BL— This fast-to-light direct dye gives bright bordeaux on cellulosic fibres. Light fastness is hardly affected by crease-resist finishes. The wet fastness of dyeings is considerably improved by after-treatment with Levogen WW, FWN or HW, but the hue becomes bluer. Good solidity is obtainable on cotton/regenerated cellulose mixtures. The wool component in wool/cellulosic mixtures is only slightly stained and this staining can be eliminated by adding Mesitol WL. Fastness figures for a dyeing on cotton aftertreated with Levogen WW include— light 5–6, washing b (60°c.) 2–3, perspiration 5.

BAYER–COLORIST NO. 8— Articles in this issue include one on continuous dyeing by the Pad–Roll method and another on the treatment of dyed cotton cloths, containing brightly coloured hues of "dead" cotton, with sodium hydroxide, e.g. a 32°Tw. solution at 20°c. for 1 hr., whereby considerable improvement in solidity is obtained.

Farbwerke Hoechst A.G.

IMPERON DYES ON COTTON PIECE GOODS— This card contains resin-bonded pad-dyeings in three depths on cotton of 17 Imperon dyes originally introduced for pigment printing. As marketed, the Imperon dyes are aqueous dispersions of the pigment and part of the resin-forming composition. The remainder is contained in the Imperon Binder FA and the padding liquor is made up of the pigment composition, Binder FA and a cross-linking agent, Imperon P. These dyes are also of interest on the newer synthetic fibres and fibre mixtures. An indication of the range of colours which may be produced is given by 36 dyeings of mixtures of dyes. Fixation is brought about by steaming 7–10 min. at 102–105°c. or by dry heat for 3–5 min. at 140–160°c. When using dry heat fixation with cellulosic fibres, Pigment Fixing Agent CI (Cassella) should be used and the Imperon P and (in certain cases) the Imperon Binder FA omitted. For maximum fastness to dry rubbing Imperon Binder FR is recommended instead of part of the Binder FA. As is to be expected, the fastness to light, severe washing (95°c.) and chlorine of these dyes is very good. Fastness to dry and wet rubbing ranges from moderate to very good and fastness to solvents is very good in the majority of cases although there are a few exceptions. Eleven of the Imperon range of pigments are also marketed free from synthetic resin as the Imperon K range and can be used with practically all oil-in-water type binders.

INDANTHREN DYESTUFFS ON COTTON— This card contains dyeings in three depths on cotton yarn of 16 Indanthren vat dyes and two others, "Vat" Scarlet GG and "Vat" Red 5B. In addition there are 20 mixture dyeings on yarn and a further 16 on cloth. The text (35 pp.) contains full details of dyeing methods, including pigmentation methods and the vat-acid process.

J. R. Geigy A.G.

IRGALAN AND IRGANOL S DYES— This new edition (1221A) of the Irgalan card (1221) contains dyeings in ten depths on wool cloth of 32 Irgalan 2 : 1 dye : metal complex dyes and 10 Irganol S neutral-dyeing acid dyes compatible with the Irgalans in dyeing behaviour and fastness characteristics and of particular value as shading colours where the metal-complex dyes cannot produce the brightness required. Mixture dyeings in five depths of forty-eight combinations of these dyes are also included. The first edition of this card described 20 Irgalans and 4 Irganol S dyes and the increase in the number of each type gives some indication of their advance in importance.

POLAR BRILLIANT BLUE 2GL— This acid anthraquinonoid dye gives bright blues on wool, silk, and polyamide fibres when applied from neutral or weakly acid dyebaths. Dyeings are considerably greener than those obtained with Brilliant Blue GRL but are comparably bright and identical in fastness properties. It exhausts better under neutral conditions than the GRL brand and is thus suitable as a shading colour with, e.g. Irgalans, and is particularly recommended where Irganol Blue BS is unsatisfactory as regards hue or levelling characteristics. Fastness figures on wool include— Light 6, alkaline milling b 4–5, washing b 4–5.

SOLOPHENYL YELLOW A3GL— An addition to the range of fast-to-light direct dyes particularly suitable for use on cellulosic materials subsequently to be crease-resist finished. It gives bright golden yellows somewhat brighter than those from the A2GL brand. It is more soluble than the latter and slower dyeing. Cellulose acetate rayon is reserved white and wool only very slightly stained under acid conditions which is particularly important when it is used for acid dyeing wool–cellulosic fibre mixtures. Fastness figures on spun viscose rayon include— Light 7, washing a (40°c.) 5, perspiration 3–4.

MAXILON DYES ON ORLON 42 YARN— This card contains fifty mixture dyeings on Orlon 42 yarn. These dyes are recommended for polyacrylonitrile fibres where good fastness to light and wet treatments is required together with a simple method of application.

The Geigy Co. Ltd.

ERIO ANTHRACENE BRILLIANT BLUES FFL AND RFF— These level-dyeing acid dyes give very bright blues of good fastness to light on wool and are particularly recommended for use on carbonised material and knitted cloths. The FFL brand is the greener and both are intended to be used only for blues, alone and in combination with each other. Fastness figures include—

	Light	Washing (S.D.C. Test 1)	Carbonising
Blue FFL	5–6	4–5	4–5
Blue RFF	5–6	4	5

Imperial Chemical Industries Ltd.

TECHNICAL INFORMATION LEAFLETS— *Dyehouse No. 500 (Replaces No. 450). Subject Index to Technical Information Leaflets (Dyehouse) Nos. 161–499.*

Dyehouse No. 512. Chrome Dyes: Application to Wool Yarn by the Afterchrome Process— It has been shown the older procedure of applying afterchrome dyes from a bath set initially with acetic acid and adding formic acid to exhaust frequently results in unlevel dyeing due to the rapid uptake of dye following the acid addition. It is now recommended that all the acid required be added, the wool entered and treated in the acid solution for 10–15 min. at 45°c. to give a uniform pH of 4·5. The dye is then added, the bath raised to the boil in 30 min. and dyeing continued for 45 min. The bath is then cooled to 80°c., the chrome added and chroming continued for 30 min. at the boil. The chrome dyes are classified according to their level-dyeing properties when applied by this method and preferred combinations of dyes for particular purposes are given.

Dyehouse No. 513 (Replaces No. 236). Light Fastness of Organic Pigments in Paint Media— Light fastness figures are given for a full range of organic pigments (except for Pure Bronzeless Blue 16266— a Prussian Blue) in an alkyd paint and a nitrocellulose lacquer according to B.S.1006 as an alternative to using the Madder Scale. The value of the latter has declined in recent years. This is one of the first attempts to use B.S.1006 for coloured pigments with the object of giving numerical light fastness ratings. The results are to be regarded as provisional until more experience has been gained.

Dyehouse No. 514. Colours for Building and Decorative Paints: British Standard 2660:1955.

Dyehouse No. 515. Printing of "Terylene"–Cellulosic Fibre Unions— Prints of good all-round fastness and solidity of colour may be obtained on a 67 : 33 Terylene–cotton mixture cloth by using selected Caledon and Durindone dyes and the Alcian "X" dyes are also of interest. Mixtures of reactive dyes or solubilised vat dyes

with disperse dyes are also of interest but the fastness obtained is generally lower.

Dyehouse No. 516. Chrome Dyes: Application to Wool Piece Goods by the Afterchrome Process— Level-dyeing chrome dyes applied by the afterchrome process are of interest for dyeing wool cloths where high fastness demands have to be met. For reasons set out in *Technical Information Leaflet No. 512* it is recommended that the cloth is run in water containing the whole of the acid required, at 45°c. for 10–15 min. to give a uniform pH 4·5 before adding the dye and then dyeing and chroming in the normal way. The range of chrome dyes has been classified according to level-dyeing behaviour when applied by this method and data for the staining of cotton, viscose and acetate rayon is also appended together with recommended combinations of dyes for particular colours.

Dyehouse No. 517. British Colour Council Accessories Colour Card for Leather, Spring and Summer, 1960.

Dyehouse No. 519. Procinyl Orange G— Procinyl Orange G is slightly phototropic, the effect being more evident in mixtures, particularly pale greys and fawns. Return to normal is extremely rapid and little difficulty should be experienced in use.

Dyehouse No. 521. Acid and Chrome Dyes: Infrared Reflectance when Applied to Wool— Materials for military purposes and for clothing for use under strong sunlight should have low and high infrared reflectance, respectively. Figures are given for the infrared reflectance of wool dyes to a range of depths with the full range of acid and chrome dyes.

Dyehouse No. 522 (British Units) Indigo on Cotton— The necessity for using a multi-dip method in order to produce deep dyeings of Indigo on cotton is outlined and full working details are given for the continuous dyeing of cotton warps.

Dyehouse No. 524. Procion–Soledon Combinations in Dyeing. Production of Yellow-green Shades on Cotton and Viscose Rayon— The Procion dyes have enabled bright yellow-greens of high light fastness to be produced on cellulosic materials, with freedom from catalytic fading, but unfortunately the blue component has been too sensitive to burnt gas fumes. By using Procion Brilliant Yellow 6G and Procion Yellow R in combination with the solubilised vat dyes, Soledon Jade Green X and Soledon Blue 2RC a full range of yellow-greens can be produced which are very fast to light, washing, and gas-fume fading and are not subject to catalytic fading. Colours based on Procion Yellow R and Soledon Jade Green X and Blue 2RC also have high fastness to hypochlorite. The reactive dyes and solubilised vat dyes are applied simultaneously in presence of salt and sodium nitrite. Alkali is added to promote reaction between the Procion dye and the cellulose, the solubilised vat dye developed in a fresh sulphuric acid bath and the final dyeing soaped off. The method may be used batchwise, semi-continuously or continuously; typical recipes are given.

Dyehouse No. 525. Dyeing of Wool–Nylon Blended Materials— The dyeing behaviour of wool/nylon mixtures is discussed and the practical behaviour of the various groups of wool dyes is considered with particular reference to production of solid dyeings on wool–nylon yarn and cloth. Details of suitable dyeing methods are given together with selections of dyes for particular purposes. Partition data for ranges of level-dyeing acid dyes and acid-milling dyes on an 80:20 wool–nylon yarn are also given. Disperse dyes are useful for building up colour on the nylon component and ratings are given for the fastness to washing, rubbing, and light of the disperse dye on the wool to facilitate dye selection.

Dyehouse No. 526 (Replaces No. 256). Hazards Associated with the Application of Shirlan to Textiles:

   (a) *Discoloration of Textiles by Shirlan*
   (b) *Loss of Effect on Sulphur Black-dyed Textiles.*

MONASTRAL FAST BLUE RF— This is a phthalocyanine pigment, somewhat greener and weaker than the LBX brand but like the latter specially modified to increase resistance to flocculation in paints, lacquers, and printing inks and exhibiting the same high order of fastness to light, solvents, and heat and stability in presence of active organic solvents.

CALAROC EU— A stable aqueous solution of dimethylol ethylene urea for dimensionally stabilising cellulosic materials, e.g. for finishes of the "wash and wear" type.

CALATAX ASX— An anti-snag finishing agent for nylon hose.

LISSOLAMINE RC— This is a new "reduction-clearing" assistant to replace Lissolamine A 50% Paste. It is a liquid and thus easier to handle. It is also of interest as a retarding agent when producing pale dyeings of Nylomine dyes on nylon.

USE OF SALT WITH PROCION DYESTUFFS— *Technical Bulletin SD 58/3 (Revised April 1959)*. Outlines methods and describes equipment for producing and storing large quantities of stock solutions.

MODE SHADES ON "COURTELLE" ACRYLIC FIBRE— This card contains twenty dyeings on Courtelle yarn produced with disperse dyes selected on the basis of good fastness to light and washing and, in the case of the deep dyeings, maximum building-up properties. A feature of this card is that both the patterns and accompanying text are arranged to slip into a pocket wallet of the familiar blue leather cloth.

SUBJECT INDEX TO DYESTUFFS DIVISION TECHNICAL PUBLICATIONS, JANUARY 1945 TO DECEMBER 1958. 5th ED. This edition supersedes and replaces all previous editions.

PROCION BRILLIANT BLUE HGR— This homogeneous reactive dye gives bright reddish blues when dyed or printed on cellulosic fibres, somewhat greener in hue than those from Procion Brilliant Blue R. In dyeing it may be applied by the normal continuous methods used with the "H" brands but having very low affinity it is very susceptible to migration. When using pad–steam fixation it is essential to add Resist Salt L to prevent chemical reduction. It may be applied on the Pad–Roll machine but its use is limited by its moderate build-up and tendency to migrate. It can also be applied by hot batchwise methods but here again the build-up is very poor. It is very useful in printing, having very good solubility and giving very stable printing pastes. Fastness figures for a dyeing on cotton include— Light (xenon arc) 5–6, washing (Test No. 5, 5 times at 100°c.) 5, peroxide bleaching 5.

PROCION ORANGE BROWN HG— This reactive dye is of interest, alone and in mixtures, on cellulosic fibres for a wide range of browns of good fastness to light and wet treatments. Its stability in print pastes is good. Fastness figures on cotton include— Light (Bombay) 5, washing (Test No. 5, 5 times at 100°c.) 4–5, perspiration 3–4.

PROCION BRILLIANT PURPLE H3R— This homogeneous reactive dye is recommended for printing cellulosic materials to give reddish purples of good fastness to washing and excellent fastness to light. It possesses good stability in print pastes and builds up to deep colours. Fastness figures on cotton include— Light (Bombay) 6–7, washing (Test No. 5, 5 times at 100°c.) 4–5, perspiration 3–4.

PROCION DYESTUFFS ON MORDANT CHROME GLOVING LEATHER— This card contains dyeings on mordant chrome gloving leather of eight Procion dyes and also four mixture dyeings. The recommended dyeing method is to dye at 55°c, in presence of a high concentration of salt (8% solution plus 20% calc. on dry weight of leather). After 15 min. sodium carbonate (12% calc. on weight of dye) is added (pH 7–8) and dyeing continued for 30 min. After dyeing the pH of the leather is reduced to 5 by rinsing in cold running water and treating with 1% formic acid (85%). The dyeings obtained are very bright, of good fastness to light and faster to wet treatments and organic solvents than dyeings produced with conventional dyes. No satisfactory method of applying the Procion "H" brand dyes to leather has yet been found.

REPRINTS—

Printers' Rollers. D. J. Coulter. *Proceedings of the Institution of the Rubber Industry*, **5**, 112 (October 1958).

Reactive Dyestuffs— A New Method of Approach to Dyeing. I. D. Rattee. *Research*, **12**, 15 (January 1959).

Dyeing of Synthetic Fibres. D. A. Garrett. *Research*, **12**, 179 (May 1959).

A Flow Equation for Pigment–Oil Suspensions of the Printing Ink Type. N. Casson. Reprinted from "Rheology of Disperse Systems", Pergamon Press, London, 1959.

Abstracts from British and Foreign Journals and Patents

The titles of abstracts may be modified. Abbreviations of names of firms are listed in J.S.D.C., **68,** *23 (Jan. 1952),*
and also, together with symbols and the periodicals abstracted, in the annual index

I—PLANT; MACHINERY; BUILDINGS

The Mangle as a Machine
E. Moss   *J. Textile Inst.*, **50** (Nov 1959) P 654–672

Two features are of paramount importance in mangling—uniformity of the nip and efficient water removal, the latter being particularly important in drying. The effects of temperature, cloth speed, load, the diameter of the bowls and the materials of which they are made are considered in relation to mangle design. Methods for testing mangle performance are described. The chief factor influencing nip uniformity is deflection of the bowls when loaded and ways of correcting or avoiding this deflection are considered in detail. The demands made in mangles for water removal and for padding, and the extent to which existing and new designs of mangle meet these demands, are discussed.   C.O.C.

Tensionless Drying on Cylinders
E. Löhmer

Melliand Textilber., **40** (Sept 1959) 1055–1057

Previous and new models of cylinder drying ranges are described in detail. Two innovations are emphasised. Firstly, introduction of sliding couplings between drive and drum ensures that the latter is just caused to rotate by the fabric, so that shrinkage on drying is automatically allowed for, and tensions leading to subsequent shrinkage are avoided. Secondly, numerous jets, emitting superheated steam at 130°c. which impinges on the fabric at right angles, result in steam economies and increased drying rates.   S.M.J.

PATENTS

Apparatus for Separating and Collecting Carbon Black (C.I. Pigment Black 6 and 7) from Hot Furnace Gases
Columbian Carbon Co.   *BP* 824,749

Pelleting of Carbon Black (C.I. Pigment Black 6 and 7)
Columbian Carbon Co.   *BP* 824,589

Drying Continuous Flexible Sheet Material
American Viscose Corpn.   *BP* 822,936

Machine in which regenerated cellulose sheeting or the like is uniformly dried by means of heated rolls and hot air currents. Means are provided to recover the plasticiser vaporised from the sheeting during drying.   C.O.C.

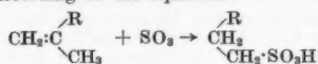Continuous Washing of Regenerated Cellulose Films and the like (XI p. 135)

III—CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

Preparation of Synthetic Detergents by Sulphonation of Olefins with a Solution of SO_2 in Liquid SO_3
K. V. Puzitskiĭ, Y. T. Eĭdus, and A. Y. Rabinovich

Zhur. priklad. khim., **32** (Aug 1959) 1819–1824

Wide fractions of the condensates of CO with ethylene, propylene and cracking kerosene give, on sulphonation with SO_3 in liquid SO_2, products whose Na salts are detergents. The reaction is carried out at −30 to −20°c., with agitation, followed by neutralisation with 20% aq. NaOH. Equimolar proportions of the reactive constituents are used. The final product is separated by evaporation of the aqueous layer. The stability of these salts to hydrolysis and the large proportion of olefins they contain suggest that they are sulphonic acids produced according to the equation

$$CH_2{:}C\!\!\begin{array}{c} R \\ \diagup \\ \diagdown \\ CH_3 \end{array} + SO_3 \rightarrow CH_2\!\!\begin{array}{c} R \\ \diagup \\ \diagdown \\ CH_2{\cdot}SO_3H \end{array}$$

T.Z.W.

Mothicidal Rhodamine Derivatives
F. J. Allan, G. G. Allan, and C. M. M'neil

Nature, **184** (21 Nov 1959) 1637

Na 2-(5′-rhodaninylidenemethyl) benzene sulphonate (I) has no mothproofing property but its *N*-ethyl and *N*-phenyl analogues have both been effective when 5% was applied to wool from a boiling bath containing 3% H_2SO_4 and 10% Na_2SO_4, though the *N*-ethyl showed signs of slight attack. The *N*-phenyl gave complete protection using 2%, and with 1% only incipient attack was seen. The improvement obtained in mothproofing properties caused by varying the N substituent in I is paralleled in studies of the bacteriotoxic and fungitoxic activity of 3-substituted rhodanines.   C.O.C.

Binders for Bonded Fibre Fabrics
N. H. Sherwood

Ind. Eng. Chem., **51** (Aug 1959) 907–910

The types of binding materials used in producing bonded fibre fabrics are reviewed briefly. Various problems associated with the binder which must be solved if the use of bonded fibre fabrics is to grow as predicted, are discussed, in particular: method of improving binder efficiency, tensile strength and colour retention, and use of solvent solutions in place of latices.   W.K.R.

PATENTS

Rotproofing Agent for Cellulosic Materials
B. F. Goodrich Co.   *BP* 823,395

Compounds of formula—

$$\cdot R^1 R^2 R^3 R^4 N \cdot S \cdot CS \cdot O \cdot Y$$
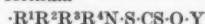
(R^1 and R^2 = CH_3; R^3 = CH_3, C_6H_5 or benzyl; or R^1, R^2, and R^3 together = hydrocarbon residue of a pyridine nucleus; R^4 = aliphatic hydrocarbon of 8–20 C, aralkylhydrocarbon, ester of a carboxy ethyl group, or *p*-diisobutylphenoxyethoxy ethyl when R^1 and R^2 = CH_3 and R^3 = benzyl, or when R^1, R^2, and R^3 are not CH_2 and Y is not ethyl or propyl may = phenyl; Y = Alk or alkenyl of 1–4 C), e.g. dimethyl cetyl benzyl ammonium alkyl xanthate, give excellent protection to cellulosic textiles and paper subjected to soil burial tests.   C.O.C.

Size for Multifilament Yarns of Synthetic Fibres
ICI   *BP* 824,138

An aqueous solution of a partly hydrolysed polyacrylonitrile or partly hydrolysed polyalkyl acrylate (Alk of 1–4) and a wetting agent is used at pH 6–8. This firmly binds the filaments together yet is readily removed by normal scouring.   C.O.C.

Antistatic Finish
ICI   *BP* 822,855

Salts with organic bases of acid phosphate esters of ethylene oxide addition products of primary aliphatic alcohols, alkyl phenols, alkyl amines, fatty acid amides or quaternary derivatives of alkyl amines applied to fibres greatly reduce the tendency to accumulate static electricity and cause no perceptible corrosion of machine parts, e.g. a spun Terylene fabric impregnated with 0·2% of the diethanolamine salt of the acid phosphate ester of the addition production of 1 mol. cetylamine with 17 mol. ethylene oxide from aqueous solution, had good antistatic properties.   C.O.C.

Solutions of Poly(vinyl Chloride)
Montecatini Societa Generale per l'Industria Mineraria e Chimica   *BP* 825,032

A mixture of trichloroethylene and nitromethane, preferably a 4 :1 mixture, is an excellent low b.p. solvent for poly(vinyl chloride).   C.O.C.

Ultraviolet Radiation Absorbers
Ward Blenkinsop & Co.   *BP* 823,544

2-Hydroxy-4-alkoxy-4′-alkylbenzophenones (Alk and alkoxy each of < 9 C), e.g. 2,4-dihydroxy-4′-methylbenzophenone, are useful ultraviolet radiation absorbers for inclusion in organic plastic materials.   C.O.C.

Caprolactam as Assistant in Dyeing or Printing Cellulose Triacetate Fibres
BrC   *BP* 823,062

Caprolactam is a very useful assistant in the application of disperse, acid or azoic dyes or oxidation bases to cellulose triacetate fibres. It is applicable in either dyebaths or printing pastes, 10–60% on the weight of water present being used.   C.O.C.

Nitrilo Methylol-phosphorus Polymers as Flame Resistant Finishing Agents

U.S. Secretary of Agriculture   *USP* 2,892,803

A mixture of a nitrilo methylol-phosphorus resin (100 parts by weight) and a water-insoluble low-decomposition-point flame retardant (5–60) which: (a) contains at least one P or S atom together with C, N, and O atoms, (b) is inert to organic textiles and nitro methylol-phosphorus resin and is thermostable and non-volatile up to 170°c., and (c) when 15% by weight is present in 8 oz. cotton twill decomposes and chars the cloth in ≯ 1 min. at 315°c. in presence of air, is used. The treated textile does not exhibit low temperature flame propagation.   C.O.C.

Gas Fume Fading Inhibitors for incorporation in Cellulose Triacetate

Celanese Corpn. of America   *USP* 2,892,672

Polymers of ethylenically unsaturated compounds containing a pyridine group, e.g. a polymer of 2-vinyl-5-methyl pyridine, are excellent gas fume fading inhibitors for inclusion in cellulose triacetate spinning solutions.
    C.O.C.

Ethylene–maleic Interpolymers as Sizes for Polyester Fibre Yarns

Monsanto   *USP* 2,892,736

Ethylene–maleic anhydride copolymers when dissolved in water at 90–95°c. have their anhydride groups hydrolysed to acid groups. Such solutions are excellent sizes for polyester fibre yarns being non-tacky even under severe humidity conditions.   C.O.C.
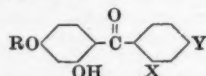
Chlorinated Benzophenone Ultraviolet Absorbers
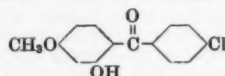
American Cyanamid   *USP* 2,892,872

Compounds of formula—

(R = Alk; X and Y = H or Cl, at least one being Cl), e.g.

are excellent absorbers of ultraviolet radiation. They are used to protect transparent, translucent or light coloured plastics.   C.O.C.

Levelling Agents for use when dyeing Nitrogenous Fibres with Metal-complex Dyes (VIII p. 132)

Tanning Agent (XII p. 135)

IV— RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

Fluorescence of Some Aromatic Compounds in Aqueous Solution

R. T. Williams

J. Roy. Inst. Chem., **83** (Nov 1959) 611–626

A review based on data obtained by means of the Aminco–Bowman spectrophotofluorometer, in which the activating light comes from a high-pressure xenon arc lamp, passes through a monochromator to isolate the required wavelength of activation, is thence directed to a soln. of the sample in a quartz cell, and the emitted fluorescence analysed by a second monochromator set at right angles to the first. Detection and estimation is possible in quantities of the order of 0·001 μg./ml. (1 in 10^{10}). It has been found that aq. soln. 10 μg./ml. of mono subst. benzenes may fluoresce under given pH conditions if they contain o-p- but not m-directing groups. Phenol in aq. soln. fluoresces in the ultraviolet at 310 mμ. and anisole at 300 mμ., supporting the view that the phenol anion does not fluoresce. Subst. nitro-groups in phenol suppress, whereas methyl groups promote, fluorescence. The dihydroxybenzenes behave similarly to phenol. Benzoic acid does not fluoresce, whereas salicylic and its m- and p-isomerides do, although unlike phenol these acids only fluoresce as ions, and the un-ionised forms of the dihydroxy-benzoic acids are practically non-fluorescent but become active when the carboxyl group is ionised. Aniline fluoresces at 340 mμ., but its cation is non-fluorescent. When another benzene ring is added to phenol either by direct linking as in the hydroxydiphenyls or by fusion as in the naphthols, the ionised forms fluoresce but not the un-ionised. 2-Hydroxyquinoline is active at 380 mμ. and this does not change in intensity or wavelength with change of pH, indicating that the fluorescence is due to the lactam (2-quinolone) form. The behaviour of 4-quinolone indicates it to be more phenolic than its 2-isomeride, while 3-hydroxyquinoline, which is one of the phenolic quinolinols, fluoresces both in acid and alkaline soln., but at slightly different wavelengths; and the 7-hydroxy-isomeride has two types of fluorescence dependent upon pH. The review ends with a discussion of data from coumarin and its hydroxy derivative.   H.H.H.

Relationship between the Absorption Spectra and Chemical Constitution of Dyes. XXX— Photoisomerisation of Azo Dyes in Aqueous Solution

M. N. Inscoe, J. H. Gould, and W. R. Brode

J. Amer. Chem. Soc., **81** (5 Nov 1959) 5634–7

Although little or no phototropism has so far been detected in solutions of p-aminoazo and p-hydroxyazo compounds in hydroxylic solvents, yet phototropic effects (undoubtedly stemming from photochemical cis–trans isomerisation) can readily be observed with p-alkoxyazo compounds. Several water-soluble methoxyazo compounds have been prepared. Their cis isomers are relatively stable in water and all showed marked changes when their aqueous solutions were irradiated. Unlike the corresponding hydroxyazo compounds, the rate of the thermal cis to trans reaction of some methoxy compounds is faster in alcohol or acetone than in water.   C.O.C.

Incorporation of N-Methyl Carbon of Monomethyl-Aminoazobenzene into Polar Dyes

H. Terayama, M. Ishidate, and A. Hanaki

Nature, **184** (7 Nov 1959) 1460–1461

The chemical binding between carcinogenic mono-methylaminoazobenzene (I) and cellular protein, which was held tentatively to be a methylene or oxymethylene, –OCH$_2$– bridge, now receives the following experimental support for the incorporation of the N-methyl group of I into the polar dyes at a position other than the 4-amino group of the dye moiety. N-^{14}C-methylaminoazobenzene is administered to rats, the polar dyes prepared, fractionated and measured by the radioactivity as well as the optical absorption, and submitted in 2 N-HCl to 'IRC-50' (H type) column chromatography. The fractions obtained afford data which are explicable on the assumption that I is further methylated in vivo via the methyl pool, which is partly endogenous and partly derived from N-methyl metabolism of radioactive I, thus forming doubly labelled dimethylaminoazobenzene, which is then metabolised in the liver. A scheme is suggested for the formation of the protein dye in vivo.   H.H.H.

Substantivity of the Acylacetarylides— III

G. Cordella

Boll. sci. fac. chem. ind. Bologna, **16** (1958) 117–121

Affinity for cotton of bisacetarylides (I) of formula R(COCH$_2$CONHC$_6$H$_4$X)$_2$ (X = Cl or H) was compared with that of the mono(acylacetarylides). This confirmed the practical value of I, particularly the terephthalic derivatives, with $-\Delta\mu_0$ being more than double that of the monoacetarylides. Substitution of heterocyclic S for O causes increase of $-\Delta\mu_0$. Results indicate that a C$_6$H$_4$ nucleus has superior substantive action to the penta-atomic nucleus. Substantivity, expressed both as % diminution of arylide in the bath and as g. arylide absorbed by 1 kg. cotton, $-\Delta\mu_0$, m.p. and absorption data are given for p-C$_6$H$_4$(C$_9$H$_8$NO$_2$)$_2$,   p-C$_6$H$_4$(C$_9$H$_7$ClNO$_2$)$_2$, aa′-C$_4$H$_2$S(C$_9$H$_8$NO$_2$)$_2$,   aa′-C$_4$H$_2$S(C$_9$H$_7$ClNO$_2$)$_2$,   aa′-C$_4$H$_2$O(C$_9$H$_8$NO$_2$)$_2$,   and   aa′-C$_4$H$_2$O(C$_9$H$_7$ClNO$_2$)$_2$, are given.

IV

Ibid., 122–5

Chem. Abs., **53** (10 Oct 1959) 18493–4

Affinity for cotton of acylacetarylide derivatives of p-phenylenediamine and benzidine has been measured. The nature and position of the acylic group exercise a notable influence on the substantivity in this order— CH$_3$ < C$_4$H$_3$O ≮ C$_6$H$_5$ < C$_4$H$_3$S. Substantivity data as above are given for p-C$_6$H$_4$(NHCOCH$_2$COCH$_3$)$_2$, p-C$_6$H$_4$(NHCOCH$_2$COC$_4$H$_3$O)$_2$,   p-C$_6$H$_4$(NHCOCH$_2$COC$_4$H$_3$S)$_2$, p-C$_6$H$_4$(NHCOCH$_2$COC$_6$H$_5$)$_2$,   (C$_6$H$_4$NHCOCH$_2$COCH$_3$)$_2$, (C$_6$H$_4$NHCOCH$_2$COC$_4$H$_3$O)$_2$,   (C$_6$H$_4$NHCOCH$_2$COC$_4$H$_3$S)$_2$, and (C$_6$H$_4$NHCOCH$_2$COC$_6$H$_5$)$_2$.   C.O.C.

Studies on Azoic Compositions. I— Solubility and Stability of Diazoamino Compound

R. Asaoka and T. Sekiguchi

Nine kinds of diazoamino compounds were prepared using Fast Scarlet G base (C.I. Azoic Diazo Component 12), Fast Scarlet GG base (C.I. Azoic Diazo Component 3), and Fast Red TR base (C.I. Azoic Diazo Component 11), as diazo components and diethanolamine, phenylglycine-*o*-carboxylic acid and sarcosine as stabilisers. The synthesis was carried out at 0–7°c. The solubility in water of the products was determined at 25°c. and thermal stability by keeping them at 30 and 50°c. for 50 hr. The products, containing sarcosine as stabiliser, had high solubility and stability.   C.O.C.

Modification of Sulphur Dyes— I

H. Rath and W. Wagner

The main constituent of Immedial Yellow GG (C.I. Sulphur Yellow 4), a sulphur dye prepared by fusing dehydrothiotoluidine with benzidine, has structural units of formula—
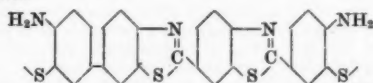
A dye molecule consists of several of these units linked by disulphide bonds. The following are also present as by-products—
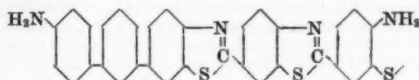
and

Reduction of the disulphide groups, present in these substances, to alkali-soluble sulphydryls is responsible for their solubility and affinity for cellulose, where the absorbed dye is fixed in an insoluble form after hydrolysis and oxidation.

Solubility of the quinoneimine dyes is brought about mainly by transition from the quinonoid to the benzenoid state.

Indocarbon CL (C.I. Sulphur Black 11)
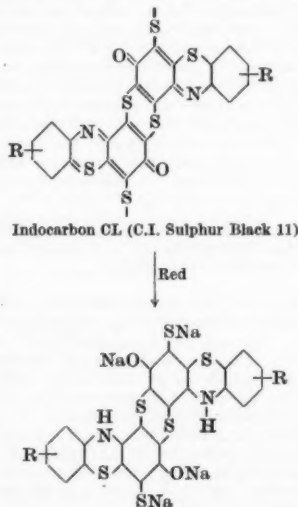
Both operations can be systematically represented by—

$$\text{Dye-S-S-Dye} \xrightarrow{\text{Red}} \text{Dye-SH} + \text{HS-Dye}$$

$$2\text{ Dye-SH} \xrightarrow{O_2} \text{Dye-S-S-Dye} + H_2O$$
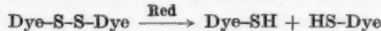
The reduction products of sulphur dyes (thiols) contain mercapto (thiol) groups. The mercapto and mercaptide compounds are highly reactive and combine quite readily with monochloroacetic acid, monochloroacetamide, ethylene chlorohydrin, ethylene oxide, and 1,3-dichlorohydrin giving compounds which in case of the quinoneimine dyes are soluble in water and in the last two instances stable in boiling acid solutions. They can be used for dyeing wool and polyamide fibres from an acid bath with good rubbing and washing fastness. The reaction can be represented by the following equation—

$$\text{Dye-S-Na} + \text{Cl-R} \longrightarrow \text{Dye-S-R} + \text{NaCl}$$

Where R is $-CH_2\cdot COONa$, $-CH_2\cdot CO\cdot NH_2$, $-CH_2\cdot CH_2\cdot OH$ and $-CH_2\cdot CH\cdot OH\cdot CH_2OH$. With ethylene oxide the reaction is—

$$\text{Dye-S-Na} + CH_2-CH_2 \xrightarrow{\text{OH}} \text{Dye-S}\cdot CH_2\cdot CH_2\cdot OH$$
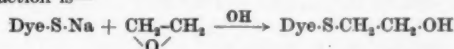
That fused sulphur dyes yield water insoluble substances on treatment with these compounds can be utilised to improve their wet fastness properties. The bifunctional products give better improvement than monofunctional, which might be due to formation of cross-linkages of the dithiols. The fused dyes can be made water soluble by sulphoalkylation, giving compounds whose aq. soln. are stable to acids. Propanol sulphonic acid, or with better results chloro- or bromoethane sulphonic acids, can be used for the purpose.

$$\text{Dye-S-Na} + Cl\cdot CH_2\cdot CH_2\cdot SO_3Na \rightarrow \text{Dye-S}\cdot CH_2\cdot CH_2\cdot SO_3Na$$
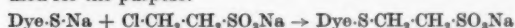
Sulphoalkylation converts both types of sulphur dyes into water soluble and stable to acid compounds, which produce dyeings on wool and polyamide fibres showing good washing and rubbing fastness. Their dyebaths are not completely exhausted because unreacted alkyl-sulphonating agent is present and this competes with the dye acid for the positively charged fibre sites. Chloromethylbenzene and the diazonium salt of *p*-aminosulphonic acid are two other roots to the manufacture of stable to acid water soluble sulphur dyes.

II
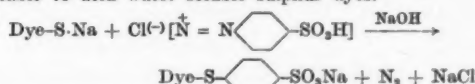
Sulphoalkylation and sulphoarylation of both types of sulphur dyes convert them into water soluble compounds. When a filtered soln. of a sulphur dye produced by reduction with glucose and NaOH is added to a hot soln. of butane sultone (1·0–1·5 g. butane sultone/20 g. dye) sulphoalkylation occurs and yields a dye applicable to wool from an acetic acid bath. The reaction is carried out in a strongly alkaline medium and proceeds by intermediate formation of an addition compound after disruption of CO_2 link.
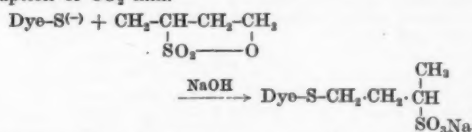
Butane sultone treatment is very simple and can be carried out in the dyebath.

A very few dye-thiols can be arylated with 1,8-naphthosultone. Better results are obtained with tolyl sultone.

Solubilisation of sulphur dyes can be effected by heating their alkyl-thioethers with dimethylsulphate in presence of soda. The process can be represented by—

The side reaction

$$(Dye \overset{\oplus}{\underset{\underset{CH_3}{|}}{S}} \cdot CH_2 \cdot R)^+ (SO_4 \cdot CH_3)^-$$

$$\longrightarrow Dye \cdot S \cdot CH_3 + R \cdot CH_2 \cdot SO_4 \cdot CH_3$$

results in a lower yield. The dyes can be applied as basic dyes. The insoluble dyes obtained by interaction of fused dye mercaptides with ethylene chlorohydrin, mono-chlorohydrin or 1,3-dichlorohydrin can be esterified with chlorosulphonic acid in pyridine, when on subsequent treatment with alkali, water soluble products showing affinity for protein fibres are obtained.

$$Dye \cdot S \cdot CH_2 \cdot CH_2 \cdot OH + Cl \cdot SO_3 \cdot N \langle \rangle \longrightarrow$$

$$Dye \cdot S \cdot CH_2 \cdot CH_2 \cdot O \cdot SO_3 \cdot N \langle \rangle \xrightarrow{NaOH}$$

$$\longrightarrow Dye \cdot S \cdot CH_2 \cdot CH_2 \cdot O \cdot SO_3Na + N \langle \rangle \xrightarrow[H_2SO_4]{H_2O}$$

$$Dye \cdot S \cdot CH_2 \cdot CH_2 \cdot OH + NaHSO_4$$

The insoluble form is restored by short treatment with 5% H_2SO_4. Chlorosulphonic acid in pyridine esterifies the chloroethylamine–mercaptide reaction product, converting it into an acid dye—

$$Dye \cdot S \cdot Na + Cl \cdot CH_2 \cdot CH_2 \cdot NH_2 \rightarrow Dye \cdot S \cdot CH_2 \cdot CH_2 \cdot NH_2 \rightarrow$$
$$\xrightarrow[Cl \cdot SO_3H]{pyridine} Dye \cdot S \cdot CH_2 \cdot CH_2 \cdot NH \cdot SO_3H + HCl$$

Butane sultone converts the aromatic and aliphatic thioethers containing an amino group into soluble acid dyes. Their dyebaths do not exhaust completely.

$$Dye \cdot S \cdot (CH_2)_2 \cdot NH_2 + \overset{CH_3}{\underset{\underset{O \underline{\quad\quad} SO_2}{|}}{CH-CH_2 \cdot CH_2}}$$

$$\longrightarrow Dye \cdot S \cdot \overset{CH_3}{\underset{}{CH}} CH_2 \cdot CH_2 \cdot SO_3H$$

Sulphur dyes suffer severe decomposition on sulphonation. But by conversion of their mercaptides into thioethers and sulphonation of the latter with 25% oleum at 80°c. a dye is produced whose ammonium salt is readily soluble in water—

$$Dye \left(S \cdot CH_2 \langle \rangle \right)_x + H_2SO_4 \rightarrow Dye \left(-S \cdot CH_2 \underset{SO_3H}{\langle \rangle} \right)_x$$

The ability of butane sultone to react with alkaline salts of aromatic and aliphatic acids by the formation of the corresponding sulphoalkyl esters is used to convert thioglycollic acid derivatives of the dyes and their condensates with p-chloromethyl benzoic acid into water soluble acid dyes—

$$Dye \cdot S \cdot R \cdot COONa + \overset{CH_3}{\underset{\underset{SO_2 \underline{\quad\quad} O}{|}}{CH-CH_2 \cdot CH_2}} \longrightarrow$$

$$\overset{CH_3}{\underset{}{}}$$
$$Dye \cdot S \cdot R \cdot COO \cdot CH \cdot CH_2 \cdot CH_2 \cdot SO_3Na$$

where R is $-CH_2-$ or $-CH_2 \langle \rangle$

These modified sulphur dyes have little importance in wool dyeing, because of their poor exhaustion and dull hues. The modification does not fundamentally change their absorption characteristics.   T.Z.W.

Absorption Spectra of Dyes. VI— Colour Change on Dry Heating of Dyed Films
Y. Ishii   *J. Soc. Textile Cellulose Ind. Japan,* **15** (April 1959) 296–300

Comparison of direct dyes on poly(vinylalcohol) and secondary cellulose acetate films. Dry heat on PVA film dyed with Benzo Azurine G causes the peak at 635 mμ. to disappear whereas no change is observed on acetate film.

Aftertreatment with aq. $CuSO_4$ partly prevents the above colour change although with other dyes there is a small general decrease in optical density on heating after such treatment. Dry heat has no effect on the spectra of films dyed with pre-formed copper-complexes. Absorption spectra of Benzo Azurine G (C.I. Direct Blue 8), Chlorazol Sky Blue FF (C.I. Direct Blue 1), and Dianil Blue G (C.I. Direct Blue 10), together with the effect of temperature, are given for the two films.   L.P.

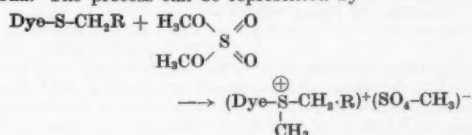### Chemistry of the Aminonaphthaquinones
E. Merian   *Amer. Dyestuff Rep.,* **48** (5 Oct 1959) 31–42

A comprehensive up-to-date review (43 references) starting from the discovery of naphthazarin (I) (5,8-dihydroxy-1,4-naphthaquinone) in 1861. A few natural dyes of I are listed, e.g. alkannin (C.I. 75530) and shikonin (C.I. 75535), and these dye alum-mordanted wool and silk violets of good fastness to light and washing, but mono-condensation products of I with aromatic amines yield after-chroming blacks of greater tinctorial strength. In general, however, β-substituted naphthazarins are tech-nically unimportant as dyes for cellulose acetate because they are not fast enough to light, and it was not until the condensation of *naphthazarin intermediate* (II) (4,8-diamino-1,5-naphthaquinone) with amines was found to give predominantly α-substitution products that progress could be made. The dicondensation products have only slight affinity, however, for cellulose acetate, whereas on polyester fibres they give greens of light fastness 4. Sulphonation of di- and tri-condensation products yields acid dyes, e.g. C.I. Acid Black 47. The monocondensation products dye cellulose acetate greenish blue, and that from II and p-phenetidine, Setacyl Blue Green BS Supra, was the first commercial member of the naphthazarin series to be used as an acetate dye. Condensation of II with aminoazo dyes yields green, yellowish green, olive, and yellowish brown dyes for cellulose acetate. Dibromination of II causes marked shift of hue to greenish blue, and the technical mixture obtained, C.I. Disperse Blue 20 (III), possesses a substantially higher affinity for cellulose acetate and polyester fibres than II itself. The higher halogenated (tri-, tetra-, etc.) aminonaphthaquinones do not dye cellulose acetate. Condensation of halogeno-II with amines gives dyes in which the α- have superior light fastness to the corresponding β-products, e.g. by reacting 6,8 - dibromo - 5 - amino - 2,3 - dimethyl - 1,4 - naphtha-quinone with arylamines, blue disperse dyes for acetate and polyester fibres are obtained, whereas the dye from 5-amino-6-bromo-8-anilino-2,3-dimethyl-4,1-naphtha-quinone, benzaldehyde and ammonia dyes these fibres fast reds, and, after sulphonation, on wool and nylon also.

The naphthaquinone system is less stable, particularly in aq. medium, than its anthraquinone analogue, a fact which explains preference for dyes of the latter class, and also for the absence of satisfactory milling dyes. On the other hand, naphthaquinonoid disperse dyes in the dissolved state in hydrophobic fibres are protected to a great extent from hydrolytic agencies and are less susceptible to gas fumes than their aminoanthraquinone analogues. For this reason, III has become important for the dyeing of acetate and polyester fibres. 9 tables of formulae of the main compounds are included.   H.H.H.

Studies on 3-(Anthraquinon-1-yl)oxazolidin-2-ones. I— 3 - (Methylanthraquinon - 1 - yl)oxazolidin-2 - ones and Their Related Compounds
K. Naiki
     Bull. Chem. Soc. Japan., **32** (April 1959) 361–365

The preparation of the following compounds is reported: 2-chloroethyl 3-methylanthraquinon-1-yl carbamate, m.p. 201–202°c. (IA), and 2-chloroethyl 4-methylanthra-quinon-1-yl carbamate m.p. 191–192°c. (IB), by the action of 2-chloroethyl chloroformate on the corresponding 1-aminomethylanthraquinone in presence of Na_2CO_3 in boiling xylene. 1-N-2-hydroxyethylamino-3-methyl-anthraquinone, m.p. 180·5–181°c. (IIA) and 1-N-2-hydroxy-ethylamino-4-methylanthraquinone, m.p. 164–165°c. by 20% aq. KOH at 107°c. on IA and IB respectively. 3-(3-methylanthraquinon-1-yl) oxazolidin-2-one, m.p. 198–199°c., and 3-(4-methylanthraquinon-1-yl) oxazolidin-2-one, m.p. 201–202°c., by 20% aq. KOH at 98°c. on IA and IB respectively, and separated from IIA and IIB which were formed simultaneously by chromatography. The properties of the various compounds are compared

with the corresponding 2-methyl compounds and steric hindrance effects attributable to the 2-methyl group are discussed.   W.K.R.
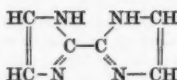
Dyes from Nitro Derivatives of Glycosines
R. Kuhn and W. Blau

Ann., 615 (1958) 108–14
Chem. Abs., 53 (10 Oct 1959) 18011–2

Blue dyes, described as di-N-oxides of the NO-indigoid class, are prepared by successive actions of (*a*) alkali and (*b*) acid on nitro-derivatives of glycosines, e.g.—

$$\begin{array}{cc} HC-NH & NH-CH \\ \parallel \quad\;\; C-C \;\;\quad \parallel \\ HC-N & N-CH \end{array}$$

Thus 1,1′,5,5′-tetranitro-glycosine heated with 2 N-NaOH gives 1,1′-dihydroxy-5,5′-dinitroglycosine; this product treated with 2 N-HCl yields the blue dye 4,4′-dihydroxyglycosine-3,3′-dioxide.   E.T.

Metal Phthalocyanines in Solutions. II— Acid-base Interaction of Some Metal Phthalocyanines dissolved in Sulphuric Acid
B. D. Berezin

Izvest. Vysshikh Ucheb. Zavedeniĭ, Khim. i Khim. Tekhnol,
2 (1959) 165–172
Chem. Abs., 53 (25 Oct 1959) 18720

Results on the solubility of metal phthalocyanine (MPc) in conc. H_2SO_4 at 25°c., according to the reaction $(MPc)_{solid} + H_2SO_4 \rightleftarrows MPcH^+ + HSO_4^-$ (I), are given in the order: initial conc. of H_2SO_4 (mole/l.), solubility $(S_{MPcH^+} \times 10^5$ mole/l.), acid function (H_0) and pK_{MPcH^+} of reaction I: For CuPc: 16·70 (time of selection 310 hr.), 102,000, −8·38, 1·81; 14·52 (40 hr.), 6520, −7·39, 2·02; 14·20 (17 hr.), 4780, −7·18, 1·94; 14·00 (30 hr.), 3650, −7·07, 1·95; 13·80 (17 hr.), 2940, −6·94, 1·91; 12·60 (840 hr.), 940, −6·27, 1·74; 12·60 (12 hr.), 990, −6·27, 1·71; 12·06 (10 hr.), 560, −5·98, 1·67; 12·06 (250 hr.), 540, −5·98, 1·69; 11·18 (10 hr.), 350, —, —; 11·18 (53 hr.), 360, —, —; 10·25 (51 hr.), 120, —, —; 9·80 (53 hr.), 110, —, —; 9·05 (30 hr.), 67, —, —; For ZnPc: 1725, 560, −8·62, 2·31; 14·52, 32·5, −7·39, 2·32; 13·17, 5·5, −6·58, 2·28; 13·10, 2·9, −6·52, 2·49; 12·33, 1·7, −6·13, 2·33; 11·61, 1·1, −5·72, 2·12; For CoPc 16·70, 295, −8·38, 2·35; 14·52, 33·8, −7·39, 2·30; 14·45, 28·8, −7·32, 2·30; 14·30, 19·2, −7·23, 2·39; 14·30, 21·9, −7·23, 2·33; 14·00, 14·0, −7·06, 2·35; 13·80, 8·6, −6·94, 2·45; 13·78, 8·1, −6·94, 2·48, 12·32, 3·2, —, —; 11·61, 1·9, —, —; For NiPc: 14·52, 252, −7·39, 1·43; 13·17, 39·4, −6·58, 1·42; 13·17, 38·9, −6·58, 1·43; 12·33, 11·9, −6·13, 1·49; 12·33, 11·8, −6·13, 1·50; 7·90, 0·37, —, —. H_2Pc, freed from the metal by the acid, is relatively readily soluble in conc. H_2SO_4 (> 8 mole/l.) and its solubility was calculated by optical d. data at 604 mμ.; 6·4 × 10⁻³ mole/l. Extinction coefficients were also determined for H_2Pc, 138 (604 mμ.), for $CuPcH^+$, 3880 (642 mμ.), for $CoPcH^+$, 5350 (642 mμ.), for $NiPcH^+$, 7530 (642 mμ.), and for $ZnPcH$, 1180 (572 mμ.). Study of the type of chemical bond in the complexes was made possible by varying the acid-base properties of the ligand during complex formation. Formation of multibonds between the metal and the ligand in NiPc and CuPc was established experimentally. On the basis of the properties of MPc, structural formulae are proposed for free H_2Pc and its covalent complex salts. These formulae are in good agreement with X-ray data.   C.O.C.

Photographic Properties of Some Symmetrical Carbocyanine Dyes having Different Alkyl groups on the Heterocyclic Atom
I. I. Levkoev and E. B. Lifshits

Zhur. Nauch. i Priklad. Fot. i Kinematografii,
3 (1958) 419–426
Chem. Abs., 53 (25 Oct 1959) 18703

Study of a series of symmetrical carbocyanine dyes having no substituents in the chain but substituted by Alk on the N atoms, showed that contrary to the literature methylates and ethylates of the dyes (with indolenine, thiazoline, benzimidazole, and thiadiazole[1,3,4]groups) have much the same sensitising action. However with thia-, oxa-, and quino-(2)-carbocyanine dyes, the NN'-dimethyl derivatives are significantly less effective than the ethyl analogues. In the character of the sensitisation spectra, fogging and desensitising action, and basicity
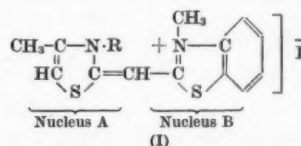
value, the methylates were very close to the corresponding ethylates. Those methylates which, in contrast to the ethylates, are adsorbed on the emulsion microcrystals predominantly in the *H* state, have significantly lower sensitising action than the ethylates. These states have such small photochemical activity that their bands are practically not observed in the sensitisation spectra. In a series of 1,1′-dialkyl-3,3,3′,3′-tetramethylindocarbo-cyanines, tendency to sensitisation of the second type increases from $CH_3 < C_2H_5 < C_3H_7$.   C.O.C.

Unsymmetrical Methin Cyanines derived from 4-Methyl-3-aryl-1,2-dihydrothiazole-2-thione
P. Tripathy and M. K. Rout

J. Indian Chem. Soc., 36 (Aug 1959) 590–592

To determine the basicity of certain heterocyclic nuclei. the prepn. and absorption and sensitisation spectra are described for 16 unsymmetrical methin cyanines of general structure I. These are obtained by the action of 3-phenyl-(or *o*-tolyl-, *m*-tolyl-, or *p*-bromophenyl) 4-methyl-1,2-dihydrothiazole-2-thione on each of the 5 heterocyclic cpd.: 2-methylbenzoxazole, lepidine, 4-phenyl-2-methyl-thiazole, and quinaldine, in presence of methyl *p*-toluene-sulphonate.

$$\left[\begin{array}{cc} CH_3\text{-}C\text{-}N\text{-}R & +\overset{CH_3}{\underset{\,}{N}}\text{-}C \\ HC \quad C\text{=}CH\text{-}C \\ S & S \end{array} \right] \bar{I}$$

$$\underbrace{\qquad\qquad}_{\text{Nucleus A}} \quad \underbrace{\qquad\qquad}_{\text{Nucleus B}}$$
(I)

(R = phenyl, *o*-tolyl, *m*-tolyl, or *p*-bromophenyl. Nucleus B = benzoxazole-2; 4-phenylthiazole-2; benzimidazole-2; quinoline-4 or -2).   H.H.H.

Synthetic Food Dyes
R. G. Olmedo and L. Villanva

I— Characteristics and Properties of the Water-soluble Dyes permitted for use in Spain
Anales bromatol. (Madrid), 11 (1) (1959) 9–47

Review of the characteristics, chemical and toxicological properties and applications of 4 yellow, 12 red, 6 blue, 3 violet, 2 green, and 1 orange water-soluble dyes permitted for use in foods or in wrappers for food in Spain.

II— Spectrophotometric study of the water-soluble dyes
Ibid., 49–108

An account of the structures, classification and light absorption curves of the above dyes.

III— Spectrophotometry of Water-soluble Red, Orange, and Yellow Dyes at Various pH
Ibid., 109–178
Chem. Abs., 53 (25 Oct 1959) 19190

The absorption maxima at various pH are given.
                    C.O.C.

Formation and Ageing of Precipitates. X— Electron Microdiffraction Study of the Crystal Habit of Precipitated Barium Sulphate (C.I. 77120)
K. Takiyama

Bull. Chem. Soc. Japan, 32 (Jan 1959) 68–70

From initially weak solutions (< 0·001 M.) $BaSO_4$ precipitates as rectangular perfect crystals but from initially stronger solutions (0·001–0·020 M.) it precipitates in dendrite forms.   C.O.C.

PATENTS

Direct Introduction of Diazonium Groups into Aromatic Compounds
J. M. Tedder   *BP* 824,489

Aromatic compounds other than primary amines react with nitrosyl derivatives of inorganic acids, in presence of an inert organic solvent if necessary, to give diazonium compounds. Mercury compounds are useful catalysts for the reaction. Thus, all parts being by weight, *p*-nitro-anisole (3·06) and mercuric oxide (0·043) are dissolved in conc. sulphuric acid (18) at 20°c. A solution of $NaNO_2$ (6·9) in conc. sulphuric acid (54) is added over 3 hr. at 20°c. After 3 hr. at 20°c. the mixture is poured on to ice (600), neutralised and filtered. The filtrate contains 2-methoxy-5-nitrobenzenediazonium sulphate.   E.S.

Diazo Component for Diazotype Printing
Kalle & Co.   *BP* 824,660

Compounds of formula—
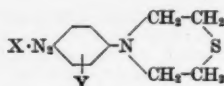
(X = acid radical; Y = H, Alk, alkoxy or Hal), e.g. the fluoroborate of the diazo compound of N-4'-aminophenyl-(1')-thiomorpholine, used as the diazo components in diazotype material yield, according to the coupling component used, very strong blues, browns or yellows of excellent covering power.   C.O.C.

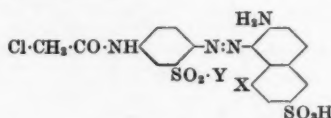## Colour Couplers
Kodak   BP 825,311
Colour couplers whose use results in images of improved heat stability are obtained by introducing into known colour couplers, in a position other than the coupling position, at least one $NH \cdot O \cdot C_n F_{2n+1}$ (n = 1–13) group.
                                               C.O.C.

Monoazo Acid Dyes having a Chloroacetamido Group
Ciba   BP 824,171
Monoazo compounds—

(Y = aryl of benzene series or $N(C_6H_5)_2$; X = H or OH) are acid dyes of better wet fastness than similar products having an unsubstituted acetamido group instead of the chloroacetamido group. Thus 2-amino-5-chloroacetamido-4'-methyldiphenylsulphone (I) is diazotised (acetone may be added to accelerate the reaction) and a mixture of γ acid and Na 1,3,6-naphthalenetrisulphonate heated to 70–80°c. is added. After 24 hr. at 30–35°c. Na₂CO₃ is added. The product (Y = p-toluyl; X = OH) dyes wool bluish red from an acid bath. Preparations of I by treating the 2,5-diamino compound with chloroacetyl chloride or chloroacetic anhydride are outlined.   E.S.

Metallisable Benzeneazodiphenylamine Disperse Dyes
Eastman Kodak Co.   BP 824,409
Suitable derivatives of o-aminophenol, o-anisidine, or o-phenetidine are diazotised and coupled with derivatives of 3-hydroxydiphenylamine—
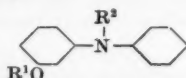
(R^1 = H, Alk, or hydroxyalkyl; R^2 = H, Alk, hydroxyalkyl, or cyanoalkyl) to give disperse dyes which may be metallised, e.g. on cellulose acetate with $Ni(SCN)_2$. Metallising in substance gives colorants which may be added to the spinning solutions of cellulose acetate, or can be applied from aqueous dispersion to wool, nylon, and polyacrylonitrile. Thus 2-amino-4-nitrophenol is diazotised and coupled with N-β-hydroxyethyl-3-methoxydiphenylamine in an acetic–propionic acid mixture to give—
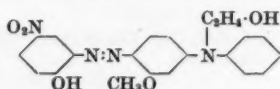
which dyes cellulose acetate orange, converted to red of good fastness to washing and light by padding with aq. $Ni(SCN)_2$ and steaming at 0–5 lb./sq. in. for 10 min.
                                               E.S.

Monoazo Disperse Dyes, and Disazo Colorants for Spin-dyeing
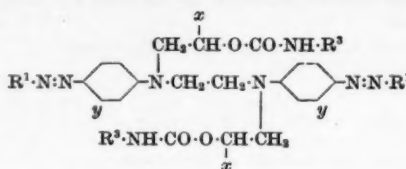S   BP 824,443
Monoazo compounds—
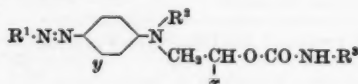
are orange to blue disperse dyes, and disazo compounds—

(R^1 = residue of isocyclic or heterocyclic diazo component free of water-solubilising substituents; R^2 = ethyl, cyanoethyl, difluoro-, or trifluoro-ethyl; R^3 = phenyl or ethyl; x = H, Hal, CH_3, C_2H_5, methoxy or ethoxy; y = H, Cl, CH_3, CF_3, methoxy, ethoxy or alkanoylamino of < 19 C) are colorants for the mass coloration of cellulose acetate. Thus diazotised 2-chloro-4-nitroaniline is coupled with the ethylcarbamic ester of N-ethyl-N-β-hydroxyethyl-m-toluidine to give—
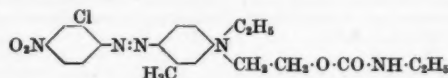

which dyes cellulose acetate and nylon scarlet from aq. dispersion.   E.S.

Blue Basic Monoazo Dyes for Polyacrylonitrile Fibres
Ciba   BP 824,280
The salts of basic compounds formed by coupling a diazotised 4-dialkylaminoaniline with derivatives of m-phenylenediamine having up to 3 alkyl groups as N-substituents dye polyacrylonitrile fibres blue, and are improved in fastness by treatment, during or after dyeing, with formaldehyde. Thus diazotised p-amino-NN-dimethylaniline is diazotised and coupled with m-amino-NN-dimethylaniline giving
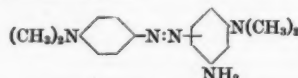
The soluble hydrochloride of this compound dyes polyacrylonitrile fibres blue from a bath containing acetic acid and formaldehyde.   E.S.

Violet to Blue-green Metal(Co and Cr)-complexes of Benzeneazothionaphthenes— Wool Dyes, and Colorants for Lacquers
BASF   BP 824,300
Anthranilic acid, o-aminophenol, o-anisidine, and derivatives of them free from SO_3H and non-complexing COOH groups, are diazotised and coupled with 3-hydroxythionaphthene or its derivatives free from SO_3H and COOH groups, and the monoazo compounds so formed are converted into the title products by treatment with Co or Cr compounds. Coupling with 3-hydroxythionaphthene-2-carboxylic acid (I) gives the same monoazo compounds, the COOH group being eliminated during coupling.
The metal-complexes formed are similar in hue to the corresponding ones given when 1-acylamino-7-naphthols are used as coupling components, but are frequently brighter.
Thus, reaction of 2-carboxyphenylthioglycollic acid with NaOH gives I, which is coupled with diazotised 2-amino-4-chloroanisole to give—
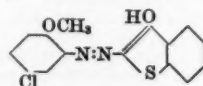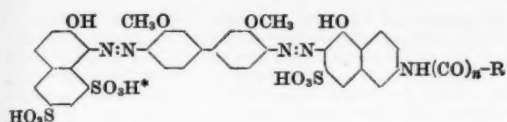

Stirring in diethylene glycol with $CrCl_3$ at 120–135°c. converts the red monoazo compound into a Cr-complex which colours cellulose nitrate lacquers reddish blue.
                                               E.S.

Navy Blue Metal(Copper)-complex Disazo Direct Dyes
Ciba   BP 824,284
The Cu-complexes derived from disazo compounds—

$(n = 0 \text{ or } 1; R = Ar$ of benzene series, free of solubilising groups) are more soluble and level better on cellulose than similar dyes without the SO_3H group marked with *, and may be mixed with such dyes to give products of satisfactory solubility and levelling properties. Thus tetrazotised o-dianisidine is alkali-coupled first with 1 mol. of G acid and then with 1 mol. of N-phenyl-J acid to give the disazo compound $(n = 0; R = \text{phenyl})$. Heating at 85–90°c. with ammoniacal $CuSO_4$ in presence of monoethanolamine gives the Cu-complex with elimination of the CH_3 groups.   E.S.

Blue Vat Dyes
BASF   *BP 825,033*

Blue vat dyes fast to chlorine and dischargeable to pure white are made by acylating 1,4-diamino-2-anthraquinonyl-anthraquinone-oxazoles with acid chlorides of poly-halogenobenzoic acid containing $\not< 2$ nuclear halogen atoms. Reaction takes place in organic solvents, e.g. nitrobenzene, at 120 to 220°c. and the product is separated by cooling and filtration. Dyes obtained are of formula—

or
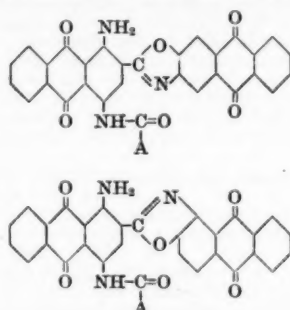
(A = phenyl radical with $\not< 2$ nuclear Hal). Fastness and dischargeability are better than for the similar dyes of *BP 436,951* and *512,580* (J.S.D.C., **52** (1936) 111, **56** (1940) 86).   E.T.

Fluorescent Brightening Agent
Ciba   *BP 823,227*

Compounds of formula—
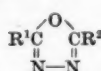
(R^1 and R^2 = aromatic radicals each containing (a) three conjugated C=C double bonds in conjugated relation with the double bonds of the oxidiazole ring and (b) a single amino group, this group being *para* to the oxidiazole ring), e.g. 2-[4'-chlorophenyl-(1')]-5-[4'-diethylamino- or 4''-dimethylaminophenyl-(1'')]-1,3,4-oxidiazole, are fluorescent brightening agents suitable for use on all fibres but particularly on wool.   C.O.C.

Fluorescent Brightening Agents for Polyacrylonitrile Fibres
Ciba   *BP 824,659*

Compounds of formula—
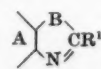
(A = subst. or unsubst. benzene radical; R^1 = radical containing at least 3 conjugated double bonds which are also in conjugation with the $>$C:N-bond of the hetero ring; B = S, O or $>NR^2$ (R^2 = H, Alk, hydroxyalkyl or aralkyl), e.g. $\alpha\beta$-di-[5-methylbenzooxazolyl-(2)]-ethylene, are fluorescent brightening agents having good affinity for polyacrylonitrile fibres from both acid and alkaline liquors.   C.O.C.

Fluorescent Brightening Agents for Use in Cosmetics
Gy   *BP 825,413*

Stilbene fluorescent brightening agents particularly those of formula—
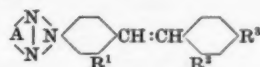
(A = naphthyl, alkoxynaphthyl, alkoxyphenyl, and alkoxyalkyl phenyl radicals, in which two vicinal C atoms of the aromatic nucleus are bound to the triazole N atoms; R^1 = H, sulphonic acid aryl ester, sulphonic acid amide, alkyl sulphonyl or arylsulphonyl; R^2 = H, alkoxy, sulphonic acid aryl ester, and sulphonic acid amide; R^3 = H, alkoxy, naphthotriazolyl, sulphonic acid aryl ester or sulphonic acid amide) are especially suitable for use in cosmetics. Thus 4-[(naphtho-1',2',4,5)-1,2,3-triazolyl-2]-stilbene-2-sulphonic acid monoethylamide enhances the luminosity of lipstick both before and after application to the skin.   C.O.C.

Heavy Metal Containing Azine Pigments
American Cyanamid Co.   *USP 2,877,252*

Stable, water-insoluble heavy metal chelates of azine derivatives are obtained by heating a metal salt of a fatty acid, e.g. cupric acetate, a hydroxyarylazine and an N-alkylamide of a fatty acid. An outstanding pigment so obtained is the chocolate-brown compound—
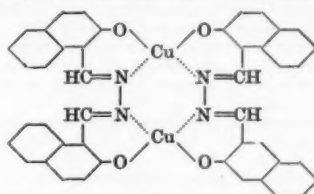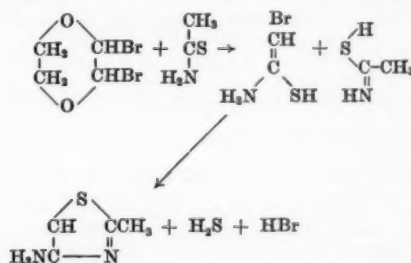

made by reacting formyldimethylamine, cupric acetate, and 2-hydroxy-1-naphthaldehyde at 110–115°c.   E.T.

Cyanine Dyes
Sperry Rand Corpn.   *USP 2,892,834*

Treating thioacetamide with a brominating agent yields a new class of thiazole bases, the reaction being—


These bases are useful intermediates for cyanine dyes. Thus treatment with an ester converts them into quaternary salts which when treated with an α-halogeno-quaternary salt in presence of an acid binding agent yield pseudocyanine dyes.

USP 2,892,835

2,7-Dialkyl-4-isopropyl-4,5,6,7-tetrahydrobenzo-thiazoles, particularly the 2,7-dimethyl compound, are similarly used to prepare cyanine dyes in which one or both of the auxochromic N atoms lie in a 7-methyl-4-isopropyl-4,5,6,7-tetrahydrobenzothiazole nucleus, e.g. the dye—
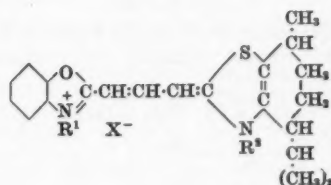
USP 2,892,836

2-Alkyl-spiro(4,5)decano(6,7d)thiazoles, particularly the 2-methyl compound—
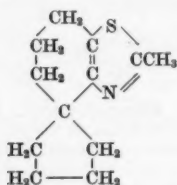
are similarly used to prepare cyanine dyes in which one or both of the auxochromic N atoms are in a spiro(4,5)-decano(6,7d)thiazole nucleus.

USP 2,892,837

Cyanine dyes in which one or both of the auxochromic N atoms are in a 4,5,6,7-tetrahydrobenzoxazole nucleus are similarly produced from 2-alkyl-4,5,6,7-tetrahydrobenz-oxazoles.

USP 2,892,838

Cyanine dyes in which one or both of the auxochromic N atoms are in a 6,7-dihydro-4-*H*-thiopyrano-(4,3d) thiazole nucleus are similarly prepared from 2-alkyl-6,7-dihydro-4-*H*-thiopyrano(4,3d)thiazoles.   C.O.C.

Siliceous Pigments for Incorporation in Rubber
Columbia–Southern Chemical Corpn.   *USP 2,892,807*

Pigments compatible with rubber to give products of improved wear resistance and tensile strength, tear and modulus properties, are obtained by treating hydrated silica with a lactone, triazine compound or epoxide.
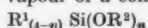   C.O.C.

Organosiloxane-coated Titanium Dioxide (C.I. Pigment White 6)
National Lead Co.   *BP 825,404*

TiO_2 is rendered both hydrophobic and lyophilic by treating it with the vapour of a compound of formula—

$$R^1{}_{(4-n)} Si(OR^2)_n$$

(R^1 = Alk, Ar or H; R^2 = Alk or H; n = 1, 2 or 3) e.g. $CH_3Si(OC_2H_5)_3$, so that the siloxane polymerises simultaneously with its deposition on the pigment.
          C.O.C.

Magnesium–Zinc Alloy Pigments
Dow Chemical Co.   *BP 823,003*

A mixture of (*a*) 80–20% by volume of a powdered alloy of 30–15% by weight of Mg and 70–85% of Zn and (*b*) 20–80% by volume of a zinc chromate or an alkaline earth metal chromate, applied in paint gives both protection against corrosion and a good appearance to iron or steel.
          C.O.C.

Grain-ripening of Inorganic Pigments
FBy   *BP 822,986*

A uniform product free from agglomerates or grit is obtained by heating a crude inorganic pigment while it is suspended in more than its own quantity of a melt made up of an alkali metal and/or alkaline earth metal halide and/or caustic alkali. This yields white and coloured pigments of hitherto unknown quality and substantially improved colouring power and brilliance. The time needed for ripening is greatly reduced, often only a few minutes heating being necessary.   C.O.C.

Fluorimetric Investigations of Fluorescent Brightening Agents (XIV p. 137)

V— PAINTS; ENAMELS; INKS

Vitreous Enamel Colouring Compositions (IX p. 133)
Vinyl Polymer Polyepoxy Coating Compositions (XII p. 135)

VI— FIBRES; YARNS; FABRICS

Thirteenth Annual Review of Materials of Construction— Fibres
C. S. Grove, R. S. Casey, and J. L. Vodonik
          Ind. Eng. Chem., **51** (Sept 1959, Part II) 1172–1175
The main developments in 1958–9 are reviewed briefly under the headings: new fibres, natural fibres, nylon, polyesters and acrylics, research, industrial uses, tyres, and non-woven fabrics. 61 references.   W.K.R.

Migration of Electrolytes into Cellulose Fibres
B. Andersson and O. Samuelson
          Svensk Papperstidning, **62** (15 Nov 1959) 775–784
Using the method described in *Svensk Papperstidning*, **61** (1958) 1001 and based on the determination of so called "salt-free" water skin in a soln. of high mol. electrolyte unable to penetrate into the interior soln. (glucose), it is shown that the concn. of electrolyte within the fibre is less than that of the external soln. not only in systems where the carboxyl groups in the cellulose are dissociated but also in acid media where the counter-ion effect can be neglected. For a rayon fibre with low swelling the value of the mean activity coefficient is of the same order of magnitude as that of a 40% glucose soln. Higher-swelling types can be compared with 25% glucose solns. The concn. of electrolyte in the cellulose phase is independent of the amount of external soln. adhering to the cellulose. (*In German*.) 15 references.   R.A.

Structural Heterogeneity in Viscose Fibres
A. Nakai
          Bull. Chem. Soc., Japan., **32** (Oct 1959) 1037–1043
Conclusions about the fine structure of standard and Toramomen type viscose fibres have been drawn from (1) observations of the dyeing properties of fibre sections and (2) a study of the structural gradient by a "peeling-off" technique using a nitration mixture. In standard viscose rayon made by spinning into a bath containing sulphuric acid, sodium sulphate, and zinc sulphate the fibre consists of four layers, both the skin and core being composed of two layers which differ in dye equilibrium absorption. Toramomen type viscose rayon which was spun from a low-alkali viscose into a zinc-free and low-acid bath has only two layers which correspond to the two layers of the skin of standard rayon. The author concludes that the main part of the skin is as crystalline as the core of the fibre.   W.G.C.

Supercontraction of Keratin Fibres by Lithium Bromide
A. E. Brown and L. G. Beauregard
          Sulfur in Proteins, Proc. Symposium, Falmouth, Mass.
          1958 (1959) 59–71
          Chem. Abs., **53** (10 Oct 1959) 18115
Supercontraction of human hair in aq. LiBr does not involve disulphide bonds and can be explained in terms of secondary bond breakdown. The initial phase of contraction in conc. soln. is reversible and probably involves cleavage of H bonds between peptide groups. In later stages of contraction, secondary bonds involving COOH and NH_2 groups are involved. At elevated temp. the peptide chains thus liberated coil because of entropy forces, the entire structure collapses, and a highly disorganised keratin is produced.   C.O.C.

Decomposition of Keratin by Micro-organisms
J. J. Noval and W. J. Nickerson
          Sulfur in Proteins, Proc. Symposium, Falmouth, Mass.
          1958 (1959) 55–7
          Chem. Abs., **53** (10 Oct 1959) 18163
Streptomyces fradiae can completely digest wool keratin at 37°c. and pH 7·7 in presence of Ca and Mg.
          C.O.C.

Donnan Theory and Uptake of Halogen Acids by Wool
Y. Takase   *J. Soc. Textile Cellulose Ind. Japan,*
          15 (April 1959) 292–295
Adsorption isotherms of pure HCl and HI on wool are determined by electro-conductivity. Saturation values of 0·85 and 0·88 respectively are obtained, and hence the pH values at 50% saturation found to be 2·3 and 2·5. Thus I⁻ has an affinity for wool relative to Cl⁻ and the Donnan theory can be written $pH_i = 2pH_\sigma + \log fa/v$ where *a* is the total concentration of H⁺ adsorbed by the fibre, *v* the volume of the internal solution and *f* a correction factor for anion affinity.   L.P.

Cystine in Reduced Wool. I— Determination of Sulphhydryl Groups
Y. Nakamura and Y. Nemoto
          J. Soc. Textile Cellulose Ind. Japan,
          15 (April 1959) 285–291
After "cold setting" of wool with mercapto-acid, the phospho-18-tungstic acid method, described by Zahn, is used to estimate total –SH content and mercapto-acid adsorbed by reduced wool. Under severe conditions of hydrolysis, values for –SH detected decrease. If the

reduced wool is heated at low temperatures –SH increases. When the –SH and –S–S– determination method is used, conditions of mild hydrolysis are preferable, e.g. 20% HCl at 105°c. for 3 hr. If untreated wool is hydrolysed in presence of mercapto-acid, a definite amount of the latter disappears.   L.P.

Swelling Behaviour of Jute in Water and Aqueous Alkali
S. C. Roy and M. K. Sen
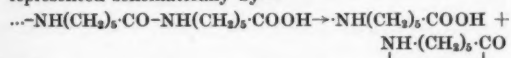
J. Textile Inst., **50** (Nov 1959) T 640–8

Measurements have been made of the transverse and longitudinal swelling of jute in water and of the absorption of water and alkali from aqueous caustic soda. That there is very little longitudinal swelling indicates restrained swelling of the structural elements of the fibre. Both delignification and alkaline treatment encourage swelling to a certain extent but whereas delignification uniformly affects both longitudinal and transverse swelling, alkaline treatment because of the accompanying disorientation markedly promotes longitudinal swelling. Compared with cotton jute has high values of absorption and swelling in dilute alkali, low values in strong alkali and maximum swelling occurs in weaker alkali. This is explained by regarding jute as having a cellulosic framework with small and/or imperfect crystals, associated with hemicelluloses and lignin which may crosslink with the cellulose.   C.O.C.

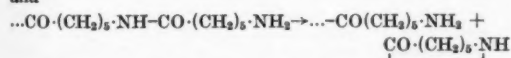## Mechanism of the Thermal Decomposition of Poly-caprolactam
H. D. Katorzhnov and A. A. Strepikheev

Zhur. priklad. khim., **32** (June 1959) 1363–1368

The speed of the thermal depolymerisation of poly-caprolactam is inversely proportional to its mean mol. wt., and directly proportional to the reaction temp. and the water content. Blocking one of the two macromolecule end groups slightly decreases the speed of the monomer formation. The rate of decomposition is greatly diminished by blocking both end groups. The imposition of the functional end groups in the macromolecule is the principle governing the mechanism of the process which can be represented schematically by—

$$...-NH(CH_2)_5 \cdot CO-NH(CH_2)_5 \cdot COOH \rightarrow NH(CH_2)_5 \cdot COOH + NH \cdot (CH_2)_5 \cdot CO$$

and

$$...CO \cdot (CH_2)_5 \cdot NH-CO \cdot (CH_2)_5 \cdot NH_2 \rightarrow ...-CO(CH_2)_5 \cdot NH_2 + CO \cdot (CH_2)_5 \cdot NH$$

Blocking of the functional end groups in the macromolecule stabilises the polymer, which does not decompose in absence of an activator (water).   T.Z.W.

PATENTS

Separating Fibres from Fibrous Vegetable Materials
R. H. Turnbull   *BP* 825,074

Modification of *BP* 721,878. The process is accelerated if treatment with the cytase liquor is carried out under fluid pressure. In addition the minimum temperature of the liquor may be reduced to 20°c.   C.O.C.

Colouring of Vinyl Polymers
Ciba   *BP* 823,257

An azine dye either directly or as a concentrated solution is incorporated into the polymer before it is processed, e.g. into fibres.   C.O.C.

Gas Fume Fading Inhibitors for incorporation in Cellulose Triacetate (III p. 124)

Combination of Re-etherification of Polycondensation during Synthesis of Polyethyleneterephthalate (XIII p. 136)

VII— DESIZING; SCOURING; CARBONISING; BLEACHING

Study of Detergents at a Solution–Air Interface by Radiotracer Method. II— The Kinetics of Adsorption of Sodium Alkyl Sulphates
R. Matuura, H. Kimizuka, S. Miyamoto, R. Shimozawa, and K. Yatsunami

Bull. Chem. Soc. Japan, **32** (April 1959) 404–407

The rate of adsorption of Na dodecyl, Na tetradecyl and Na hexadecyl sulphates at the solution–air interface measured by a radiotracer method showed that surface

excess of the detergent was proportional to the conc. of solution and the square root of the time of ageing at the initial stage of adsorption. The results cannot be explained by the simple diffusion theory. Presence of an energy barrier is suggested and values of this have been calculated for the three detergents.   W.K.R.

Tensile Strength Changes due to Hypochlorite Bleaching
L. F. McDonnell and M. N. May

TAPPI, **42** (July 1959) 526–534

The major chemical changes when chlorinated and extracted NSSC aspen pulp is treated with hypochlorite are delignification and reduction in the D.P. of pulp. Swelling, deshiving, and fibrillation result in increase in hydrodynamic specific surface area. Increase in bonding strength per unit area of handsheets is greater than increases in surface area and bonded area, suggesting that bleaching provides surfaces better capable of bonding. Bleaching is also responsible for decrease in fibre strength and in D.P. of the pulp. Correlation between fibre strength and pulp D.P. may be a forced correlation because the loss in fibre strength may in part be attributable to other sources. Hypochlorite bleaching increased the breaking length of handsheets from unbeaten pulp because of increased inter-fibre bonding strength. 31 references.
    R.A.

Chlorite Bleaching Without Chlorine Dioxide Odour
K. H. Lange and H. Bergs

Melliand Textilber., **40** (Oct 1959) 1179–1183

Theory and practice are reviewed in detail, and many practical examples are given. Materials of construction include not only Cr/Ni/Mo steel with ≮ 2% Mo, but also pitch pine. HCOOH is less corrosive than HCl. Ortho-phosphates are stabilising buffers, preferable to pyro-phosphates and polymetaphosphates as these can enhance corrosion. In long liquors (1 : 3 to 1 : 30) 0·5–6·0 g. NaClO₂ per litre are customary, in impregnation bleaching 8–25 g. per litre at a liquor ratio of 1 : 1. In long liquors wetting agents producing foaming largely prevent ClO₂ evolution. In impregnation, but not in long liquors, Axil C (FBy) combats objectionable odours effectively. Alkaline liquors of greater stability are usable, as Axil C develops an acid reaction only above 70°c. Bleaching can therewith be completed in 1 hr. at 100°c. instead of 4 hr. at 70–75°c., and greater whiteness is obtained.   S.M.J.

Effect of the Continuous Sodium Chlorite Bleach on the Degree of Polymerisation of Cotton
G. Rösch   *Deut. Textiltech.*, **9** (1959) 263–6

Chem. Abs., **53** (10 Oct 1959) 18491

Bleaching cotton cloth by impregnating with aq. NaOCl₂ of various strengths and steaming for various times showed the best white was obtained by steaming for 1 hr. at 100°c. Evolution of ClO₂ was greatest at pH 4·2, which was maintained by acetic acid. Of seven activators tested, 5 g./l. of NH₄H₂PO₄ and 3 c.c./l. of 30% H₂O₂ gave the best results. Below 2% strength NaClO₂ caused only slight changes in the polymerisation of the cellulose. Higher strengths caused damage, even complete dis-integration of the cloth.   C.O.C.

Degradation of Fibroin during the Degumming of Silk
G. Centola and P. Moruzzi   *Boll. Ass. It. Chim. Tess. e Col.*, 8 (Series II) (Sept/Oct 1959) 90–97

Measurements of the viscosity of fibroin in 4% aq. LiBr indicate some relationship between the degree of degradation of fibroin and the pH at which degumming is carried out.   C.O.C.

Pulp Bleaching with Sodium Chlorate (XI p. 135)

VIII— DYEING

Studies on the Interaction of Surface Films with Solute in Solution. V— Deposition of Monolayers of Several Amphipathic Compounds from Surfaces of Aqueous Solutions of Congo Red (C.I. Direct Red 28) and Crystal Violet (C.I. Basic Violet 3)
M. Muramatsu

Bull. Chem. Soc. Japan, **32** (April 1959) 391–395

Built up films of stearic acid, cholesterol and octadecyl-amine were obtained by depositing on to the solid phase, monolayers from the surfaces of water and, more easily,

aqueous solutions of Congo Red. Deposition of monolayers of cetyl alcohol, ethyl stearate, and ethyl-n-hexadecyl ether from either substrate was unsuccessful. Only stearic acid monolayers were obtained from Crystal Violet solution. The apparent spacing of the films indicated an attachment of dye to the film substance.   W.K.R.

Dyeing in Polymer Solutions. I— Direct Dyeing in Polymer Solution. 1
Y. Suda and T. Shirota

J. Soc. Text. Cellulose Ind. Japan, 15 (Aug 1959) 670–6

Direct Scarlet B (C.I. Direct Red 37) and Chrysophenine G (C.I. Direct Yellow 12) were dyed on viscose staple fibre from solutions of Na alginate and Na carboxymethyl-cellulose as polymer electrolytes. It was found that (1) cations dissociated from the polymer electrolyte take part in dyeing as well as those from the inorganic electrolyte; (2) the polymer electrolyte itself absorbs dye and so both the apparent concentration of dye in the solution and dye absorbed in fibre decrease; (3) Increased additions of salt cause decrease in (1) and increase in (2); (4) the reciprocal correlation between (1) and (2) causes characteristic change of the equilibrium and diffusion coefficients.   C.O.C.

Rate-of-dyeing Equation for a Finite Dyebath of Rising Temperature
K. Tsuda

J. Soc. Text. Cellulose Ind. Japan, 15 (Aug 1959) 663–9

The rate-of-dyeing equation in a finite dyebath of rising temperature is obtained theoretically by use of Crank's diffusion equation for the infinite dyebath (*Phil. Mag.*, 39 (1948) 362). Then the formula for the rate-of-dyeing equation in a finite dyebath at rising temperature is derived from Vickerstaff's hyperbola equation. The curves so obtained are compared with those obtained from experimental values obtained by dyeing 6-nylon yarn with disperse dyes. Then Duhamel's theorem is used to obtain the rate-of-dyeing equations for a finite dyebath (Wilson, *Phil. Mag.*, 39 (1948) 48; Crank, *loc. cit.*) are derived from those of an infinite dyebath obtained by Hill (*Proc. Roy. Soc.*, 104B (1928) 65) and Crank (*loc. cit.*).   C.O.C.

Influence of the Depth of a Dyeing on its Light Fastness
Ya. A. Legkun

Zhur. priklad. khim., 32 (July 1959) 1560–1563

Pale-blue direct dyeings on viscose rayon staple yarn fabric fade quicker in sunlight than deep dyeings. At the same time the destruction of the dye proceeds much faster at the beginning of the exposure. This may be the result of the protective action the dye photodecomposition products exert on the parent dye or of similar action exercised by the cellulose degradation products. T.Z.W.

Kinetics of Dyeing with Remazol (FH) Dyes
E. Bohnert and R. Weingarten

Melliand Textilber., 40 (Sept 1959) 1036–1042

Exhaustion and fixation increase with decreasing liquor ratio, dye concn., and temperature, and with increasing electrolyte concn. (Na_2SO_4). The latter promotes migration of OH^- ions into the fibre, increasing its pH relative to the liquor. S, the fraction of total dye driven on to the fibre by 50 g. Na_2SO_4 per litre, varies from 0·186 to 0·040 for 9 Remazol dyes under given conditions. Relative diffusion coefficients D^* are derived by squaring the slope of the straight line obtained on plotting C_t/C_∞, exhaustion as a fraction of equilibrium exhaustion, against $\sqrt{t}$, where t signifies dyeing time. D^* ranges from 7·8 to 0·9 for the 9 dyes. The slope is unaffected by electrolyte concn. Rate of hydrolysis is similarly unaffected thereby. Velocity constants for hydrolysis ($K_H = \log_e 2/t_\frac{1}{2}$) range from 0·0217 to 0·0077 at 60°c. with 10 g. Na_2CO_3 per litre. Half-life times are trebled by lowering pH from 10·6 to 10. Type of alkali also matters. Activation energies for hydrolysis range from 26·2 to 16·0 kg.cal./mol. For the dye–fibre reaction with a pad–jig procedure at 60°c., velocity constants K_F range from 0·240 to 0·035, and activation energies from 15·8 to 9·2. Hydrolysis increases faster than fixation with rising temperature. Actual percentage fixation, ranging from 62 to 8, is not readily related to activation energy. The ratio of velocity constants for fixation and hydrolysis, K_F/K_H, also does not tally with the order of yields. But good correlation with fixation in practice is obtained on tabulating $K_F/K_H \times D^* \times S$. Only Remazol Black B, which possesses two reactive groups, is displaced slightly.   S.M.J.

Disperse Dyes on Cellulose Acetate
K. Odajima

V— Colour after Dyeing

J. Soc. Textile Cellulose Ind. Japan, 15 (April 1959) 301–305

Effect of dye concentration on hue, and the relation between luminosity and purity, are studied by the chromaticity diagram. The colour is measured by an automatically-recording colorimeter. The first effect of increasing dye concentration is to increase the purity of the colour, but this decreases after a maximum is reached (usually 1–2% dye concentration). Curves showing the relation between luminosity and purity are given and enable comparison of the brilliancy of dyes of similar colours to be made. In general, the rate of decrease in luminosity falls with increasing concentration and the hue tends to change.

VI— Luminosity and Fibre–Dye Concentration
Ibid., 305–307

Log $Rd = k \log c + \log p$ where Rd is the luminosity of the dyed fabric, c the concentration of dye in the fibre, k and p constants, luminosity gradient and standard luminosity respectively.   L.P.

Dyeing Synthetic Fibres. IV— Dyeing Nylon with Leuco Esters of Vat Dyes
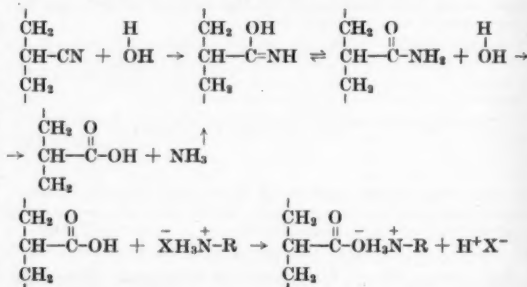V. F. Androsov and A. A. Kharkarov

Izvest. Vysshikh Ucheb. Zavedeniĭ, Tekhnol., Tekstil. Prom. (2) (1959) 110–116

Chem. Abs., 53 (10 Oct 1959) 18490

Evidence which suggests that the dyeing of nylon with leuco esters of vat dyes is of acid dyeing type.   C.O.C.

Dyeing Nitron Fibre with Basic Dyes
E. S. Roskin, A. A. Kharkharov, and A. L. Shapiro

Zhur. priklad. khim., 32 (July 1959) 1569–1575

Dyeing of polyacrylonitrile fibre with basic dyes takes place according to a scheme postulated by A. E. Poraĭ-Koshits, which can be represented as follows—

$$\begin{array}{l} CH_2 \quad\quad H \quad\quad CH_2\,OH \quad\quad CH_2\,O \quad\quad H \\ | \quad\quad\quad | \\ CH\text{-}CN + OH \rightarrow CH\text{-}C{=}NH \rightleftharpoons CH\text{-}C\text{-}NH_2 + OH \rightarrow \\ | \quad\quad\quad\quad\quad\quad | \quad\quad\quad\quad | \\ CH_2 \quad\quad\quad\quad CH_2 \quad\quad\quad CH_2 \end{array}$$

$$\begin{array}{l} CH_2\,O \\ | \quad || \\ \rightarrow CH\text{-}C\text{-}OH + NH_3 \\ | \\ CH_2 \end{array}$$

$$\begin{array}{l} CH_2\,O \quad\quad\quad\quad\quad CH_2\,O \\ | \quad || \quad\quad\quad\quad\quad\quad | \quad || \\ CH\text{-}C\text{-}OH + \,^-XH_3\,^+N\text{-}R \rightarrow CH\text{-}C\text{-}OH_3N\text{-}R + H^+X^- \\ | \quad\quad\quad\quad\quad\quad\quad\quad\quad | \\ CH_2 \quad\quad\quad\quad\quad\quad\quad CH_2 \end{array}$$

The dyeings of the 300% stretched fibre were carried out by immersing it into a dyebath containing (on wt. of fibre) 5% dye, 10% CH_3COOH (glacial), 0·5% CH_3COONa and 1% dispersing and surface-active agent (OP–10). Liquor ratio 50:1. The material was entered into the dyebath, which was raised to the boil in 20 min., and boiled for 1 hr. The fibre was then washed in cold water, soaped for 10 min. at 80°c. in 3 g./l. soap soln. and rinsed with cold water. It was noticed that the dyebath was almost exhausted in a few minutes. The speed of dyeing is determined by the force of electrical attraction between the dye and the fibre, and to a smaller degree by the speed of internal diffusion. The equilibrium is reached in 1 hr. at 100°c. The exhaustion rate is not influenced by the dye concentration. The rise in temp. causes disaggregation of the dye molecules and increases the speed of their thermal movement thus increasing the rate of the internal diffusion. Presence of CH_3COONa decreases the charge on the fibre because of absorption of Na^+ and therefore decreases the dyebath exhaustion. Acetic acid has the opposite effect.   T.Z.W.

PATENTS

Levelling Agents for use when dyeing Nitrogenous Fibres with Metal-complex Dyes
FBy   BP 824,459

A mixture of a polymeric N-vinyl-lactam with an ammonia-formaldehyde, -acetaldehyde or -butyraldehyde

condensate, e.g. polymeric *N*-vinylpyrrolidone and hexamethylene tetramine, is an excellent levelling agent when applying 1 : 1 metal-complex dyes free from acid water-solubilising groups to wool, silk, nylon or the like.   C.O.C.

Dyeing Hair and like Keratinous Materials
Société Monsavon l'Oréal   *BP* 823,503
Modification of *BP* 797,174 (J.S.D.C., **74** (1958) 670). The hair is impregnated with 5,6-dihydroxyindole at pH $\geqslant$ 7 and then treated with an aqueous solution ofan oxidising agent.   *BP* 824,519
Modification of *BP* 710,134 (J.S.D.C., **70** (1954) 374, 450). Treating the hair first with an aqueous solution of 1,2,4-trihydroxy benzene or a 5-substituted derivative thereof and then with an aqueous ammoniacal solution of an oxidising agent results in quicker dyeing and requires less strict control than the original method.   C.O.C.

Dyeing and Setting Oxidised Keratinous Fibres
P. Flesch   *USP* 2,892,756
Treatment with acid solutions of pH 2·0–3·8 renders oxidised keratinous fibres, e.g. peroxide bleached human hair, capable of being dyed level with FD&C or D&C dyes in presence of a thioglycollate and without becoming brittle or matted. Such treated fibres can also be permanently set with thioglycollate preparations.   C.O.C.

Colouring of Cellulose–Cellulose Triacetate Textiles
Celanese Corpn. of America   *USP* 2,892,668
Heating cellulose triacetate fibres so that they develop a crystalline structure, e.g. by heating at 210–220°c. for 5–30 sec., renders them resistant to mercerising lye and vat dyes. This is made use of to enable blends of cotton and cellulose triacetate fibres to be treated so that the cotton is mercerised and vat dyed while reserving the triacetate component.   C.O.C.

Use of Buffer Solutions when applying Phloroglucinol as a Developer for Diazotised Direct Dyeings
Whiffen & Sons   *BP* 823,446
Treating a diazotised direct dyeing with a solution of a partly neutralised weak organic acid before or in conjunction with coupling with phloroglucinol results in the coupling bath becoming colourless so that it may be used for subsequent processing, e.g. soaping, of the material being dyed. Thus acetate lock-knit fabric was dyed with Dispersol Diazo Black 2B (C.I. Disperse Black 2), diazotised, treated for 5 min. at 20°c. in anhydrous Na acetate (60 g.) and 30% acetic acid (60 ml.) in water (60 litres), coupled with phloroglucinol, the bath neutralised with ammonia followed by soaping the fabric in the same bath. A black of good penetration and fastness was obtained.   C.O.C.

Carriers for use when dyeing Polyester Fibres with Disperse or Azoic Dyes
FH   *BP* 824,269
Benzoic esters of aromatic alcohols, phenols or naphthols, e.g. phenyl or benzyl benzoate, used as carriers for disperse dyes, and azoic diazo components result in deeper dyeings of improved fastness to washing.   C.O.C.

Dyeing and Crimping Continuous Filament Yarns
British Nylon Spinners   *BP* 824,709
Multifilament yarn of nylon or other thermoplastic material is given a high twist, wound on to a perforated or coil-spring cylindrical bobbin, dyed at the boil preferably under pressure of 4 lb./sq.in. and then back-twisted to its initial value of twist.   C.O.C.

Colouring Glass Fibres
Fran   *BP* 825,010
Ionisable water-soluble chromiferous complexes of dyes containing the complexing metal and the dye in the cation readily dye glass fibres from aqueous solution, in some cases the bath being completely exhausted.   C.O.C.

Dip-staining of Poly(vinyl Acetal) Sheets
Pittsburgh Plate Glass Co.   *BP* 824,388
A solution of a pyrazolone azo dye containing no sulphonic acid group and a non-ionic wetting agent dissolved in water (23–27% by vol.) and alkylene glycol

monoethyl ether (73–77) is used at pH 9·0–10·5. Suitable dyes include C.I. Solvent Yellow 40, C.I. Disperse Red 15, and Nacelan Blue KB (NAC). The dyeings obtained have excellent fastness to light.   C.O.C.

Caprolactam as Assistant in Dyeing or Printing Cellulose Triacetate Fibres (III p. 123)
Dichroism of Dyes in Stretched Poly(vinyl Alcohol) Sheets. II— Relationship between the Optical Density Ratio and the Stretch Ratio and an Attempt to Analyse Relative Directions of Absorption Bands (XIII p. 136)

IX— PRINTING

Cloth Printing in Normandy in the 17th and 18th Centuries
P. Dardel   *Teintex*, **24** (15 April 1959) 247–264

PATENTS

Polychromatic Photomechanical Printing
Société Imprimerie Cino Del Duca   *BP* 825,093
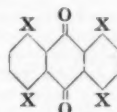
Antistain Agents for Colour Photography
Kodak   *BP* 825,421

Coloured Photographs
Polaroid Corpn.   *USP* 2,892,710
Compounds of formula—

(at least two X's = OH or NH_2 and the remainder = H, OH or NH_2), to which one mole of H has been added are developers for silver halide photographic emulsions, any unoxidised portion of the compounds remaining after development are used to provide a coloured image. Thus a baryta base is coated with leucoquinizarin dissolved in aqueous cellulose acetate hydrogen phthalate, dried and then a silver iodobromide emulsion is applied. The coated base is then exposed and wetted with an aqueous composition containing sodium carboxymethyl cellulose, NaOH, phenylethyl alcohol, and *p*-methylaminophenol as the exposed base is placed on an image receiving element. This element is a poly(vinyl butyral)-coated baryta paper coated with a 20% solution of Vinylite 28–18 (Carbide and Carbon Chem. Corpn.) in acetone, the solution containing benzoyl peroxide as catalyst. After an imbibition period of 1 min. the image receiving element is separated and is found to bear a yellow, positive dye image.   C.O.C.

Xerographic Toner
Haloid Xerox   *USP* 2,892,794
A toner usable with either of two carrier components so that it may be used in either the reversal or the direct process consists of powdered, pigmented styrene resin and as modifier to prevent smearing or removal from the carrier 0·5–2·0% of a nitrogenous compound, particularly Nigrosine (C.I. Solvent Black 7), Iosol Black (C.I. Solvent Black 13), and Luxol Fast Blue (DuP).   C.O.C.

Vitreous Enamel Colouring Compositions
DuP   *USP* 2,892,734
Colour compositions applicable in rapid succession without affecting previously applied colours, which need neither melting before application nor drying between successive applications are obtained by mixing a glass frit, an inorganic pigment and a polymerisable liquid vehicle that rapidly sets when in contact with a catalyst. Thus a polymethane mixed with glass frit and inorganic pigments is screen printed on to glass and is then sprayed with a 40% aqueous solution of ethylene diamine. This sets the enamel in 3 sec. Additional colour can be immediately applied and finally the whole is fixed to yield a clear bright glossy vitreous enamel print on the glass.   C.O.C.

Caprolactam as Assistant in Dyeing or Printing Cellulose Triacetate Fibres (III p. 123)
Diazo Component for Diazotype Printing (IV p. 127)

X— SIZING AND FINISHING

Crease-shedding Finish by use of Urea–Formaldehyde Resin. 12— Mechanism of the Crease-shedding Finish obtained with Dimethylolurea
M. Hida, S. Nimo, and Y. Nagata

J. Soc. Text. Cellulose Ind. Japan, 15 (Aug 1959) 656–662

Study of the relationship between the physical properties, e.g. recovery from creasing, imbibition value, and elastic recovery, of viscose rayon fabric given a dimethylolurea finish, and the changes in these properties on repeated soaping indicate (1) compared with the same fabrics treated with formaldehyde instead of resin, increase of elastic recovery was relatively small and presumably not caused by crosslinking between the resin and the cellulose. Perhaps the improvement in crease-shedding property is caused by deposition of resin in the fibre. (2) Surface resin, readily removed by soaping, contributes to a limited extent to the improved crease-shedding properties although the main effect is caused by resin inside the fibre.   C.O.C.

Crease Resistance Improvement of Regenerated Cellulose by Condensing Resins in Saturated Steam
E. Elöd and D. Herion

Melliand Textilber., 40 (Sept 1959) 1058–1068

This is a detailed and extensive investigation of the condensation of urea–formaldehyde resin in substance and on viscose rayon, with 22 tables of results, 9 diagrams, and 48 references. Conditions for preparing stable pre-condensates are established, the equilibrium character of the reaction is proved, and it is shown that complete condensation can take place at room temp. Equilibration is favoured by water, which promotes uniformity of molecular size, condensation between hot metal plates gives better crease resistance and lower abrasion losses than normal processing. At room temp. better effects are also obtained, but resistance to washing is lowered. The advantages of condensing in steam or superheated steam are confirmed. Analytical methods for nitrogen, free formaldehyde, and methylol groups are critically evaluated.   S.M.J.
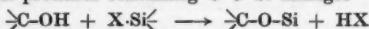
Water-repellent Finish on Cellulosic Materials by use of Organosilicates
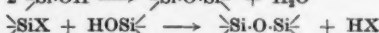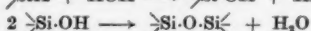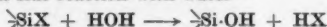M. G. Voronkov and N. V. Kalugin

Zhur. priklad. khim., 32 (July 1959) 1581–1586

Organosilicates containing –OH, H or Cl groups adjacent to the Si atom easily combine with hydroxyls of organic compounds, e.g. cellulosic fibres forming condensation products containing C–O–Si linkages:—

$$\text{>C-OH} + \text{X·Si<} \longrightarrow \text{>C-O-Si<} + \text{HX}$$

where X is ·O·CO·R, H or Cl. By this means a hydrophobic film is formed on the fibre, whose water repellent property is caused by the orientation of the hydrocarbon radical, which is away from the surface of the yarn, and also by blocking of some of the hydroxyl hydrophylic groups of the cellulose. It is not true that the water repellency results from Si–H linkage oxidation, as the action takes place with equal speed in absence of O_2 or an oxidising agent, and is catalysed by salts of Zn, Cd, Mg, Co, and Ni. Organosilicates having no functional group able to combine with cellulose do not produce stable results. A better finish is obtained on kier boiled and bleached cellulose, because its –OH groups are freed from pectin, acid residues, wax, etc. Organosilicates having a reactive group adjacent to Si atom can take part in a detrimental side reaction with water—

$$\text{>SiX} + \text{HOH} \longrightarrow \text{>Si·OH} + \text{HX}$$
$$2\text{ >Si·OH} \longrightarrow \text{>Si·O·Si<} + H_2O$$
$$\text{>SiX} + \text{HOSi<} \longrightarrow \text{>Si·O·Si<} + \text{HX}$$

(X = H, ·O·CORCl etc.), and so treatment in an inert solvent gives better results. For good water repellent treatment a mixture of tri- and difunctional organosilicates, of the respective types $R·SiX_3$ and $R_2·S·X_2$ should be used.   T.Z.W.

New Approach to Fabric Pest Control
R. J. Pence

Soap Chem. Specialities, 35 (8) (1959) 65–8, 105–6
Chem. Abs., 53 (25 Oct 1959) 19284

The nutrient value of contamination as a food source for fabric pests was investigated and divided into direct and indirect categories. The rôle of vitamin synthesis by micro organisms is the source of indirect contamination. In both categories the yields of nicotinic and pantothenic acid are vital to fabric pest development. Antimetabolites were tested as a control measure to inhibit these vitamins. These growth factor analogues, when incorporated into a fibre diet, caused the feeding insects to die of starvation.   C.O.C.

Technological Assessment of some Chemical Finishing Treatments of Caprolactam Staple Fibres
E. Fritzsche and A. Wicklein

Faserforsch. und Textiltech., 10 (Oct 1959) 475–485

Theoretical principles are summarised. Known methods are examined for applicability to caprolactam staple fibres. Finishing processes covered by over 30 patents are summarised in tables. Experiments on pilot plant scale with sulphuric acid, zinc chloride, lactam, and phenol are described and their applicability on a large scale is discussed.   W.R.M.

Pilling and its Prevention
F. Belleli   *Bull. Centre Recherches Bonn.*, (5) (1959) 5–8

Tendency to pill is connected with inter-fibre friction in that a higher coefficient of friction decreases this tendency. To test this hypothesis the following experiments were carried out: Three samples of the same Orlon knit fabric were given three different degreasing treatments using respectively: trisodiumphosphate followed by three soapings, extraction with alcohol, and a commercial detergent. Tendency to pilling decreased in the first two cases, but increased in the last. This increase is probably caused by the commercial detergent, although removing grease, itself being partly deposited on the fibre and acting as a lubricant. Further experiments showed that the first two treatments increased the coefficient of friction while the last decreased it. The last set of experiments using wool/synthetic fibre unions (three samples containing three different types of synthetics) proved again the connection between coefficient of friction and the tendency to pill. Inter-fibre friction is not considered to be the only factor, the importance of fibre flexibility and elasticity being stressed.   W.M.

PATENTS

Improving the Resistance of Wool and/or Nylon Fabric to Pilling
Maifoss   *BP* 823,048

The fabric is treated at pH 2–5 and 150–212°F. in an aqueous liquid containing a formaldehyde-aromatic sulphonic acid condensate and a non-ionic dispersing agent or water-repellent liquid polysiloxane. The process can be carried out in the same bath and at the same time as acid dyeing.   C.O.C.

Setting Fabrics containing Yarns of an Acrylonitrile–Vinylidene Chloride Copolymer
BrC   *BP* 823,247

Fabrics containing yarns of an acetone-soluble acrylonitrile–vinylidene chloride copolymer are set by treatment with dry heat at 110–150°c. or with water or steam at ⊁ 115°c.   C.O.C.

Rendering Polyacrylonitrile Fibres Antistatic
British Nylon Spinners   *BP* 824,125

Treatment of polyacrylonitrile fibres with warm aqueous alkaline hydrogen peroxide considerably reduces the resistivity of polyacrylonitrile fibres and so their tendency to become electrostatically charged.   C.O.C.

XI— PAPER AND OTHER CELLULOSIC PRODUCTS

Waterproofing Paper with Alkylacetoxy-silans and -siloxans

M. G. Voronkov, V. P. Davȳdova, and N. P. Grishanine

Zhur. priklad. khim., **32** (May 1959) 1106–1112

Some alkylacetoxy-silans and -siloxans can be satisfactorily employed for waterproofing paper. Best results were obtained with a $1:1\cdot2$ mol. mixture of dimethyldiacetylsilan and tetraacetylsilan. Their good waterproofing action results from them forming linear polymers of the type $-O\cdot SiR_2-[O\cdot Si(O\cdot CO\cdot CH_3)_2-O-SiR_2]_n-O-Si(O\cdot CO\cdot CH_3)_2-O-Si(O\cdot CO\cdot CH_3)_2-[O-SiR_2-O-Si(O\cdot CO\cdot CH_3)_2]_n-O-SiR_2-O-SiR_2-$ ($R = CH_3$ or C_2H_5). The treatment did not impair the quality of the paper and in some cases improved it. The process was carried out in a 2·5% soln. of the polymer in toluene for 1 hr., followed by heating the treated material for 3 hr. at 105–110°C. This time was shortened to 20–30 min. at 105–110°C., or to 2 min. at 150°C., by addition of 0·1% of $Ti(O\cdot C_2H_5)_4$.   T.Z.W.

Pulp Bleaching with Sodium Chlorate

W. H. Rapson, C. B. Anderson, and R. W. Millen

TAPPI, **42** (Aug 1959) 642–649

Direct bleaching with sod'um chlorate without a catalyst requires very high acidity which causes severe degradation of the pulp. The use of vanadium catalyst speeds up the reaction at acidity ranges where the damage by hydrolysis and oxidation is acceptable when strength is not a major consideration. Increased consistency, lower temp., and a bleaching time of several weeks gives very high brightness levels in partly bleached pulps, using vanadium catalysed chlorate. In the case of unbleached pulps the steeping time must be reduced to a few days to avoid excessive degradation. Small amounts of sodium chlorate added to chlorine has little effect without catalyst. Larger amounts of chlorate reduces the viscosity appreciably. Chlorine dioxide gives higher maximum brightness with no significant degradation of the pulp. 13 references.   R.A.

Yellowing of Pulp during Mercerising

P. Sarten and S. Wirheim

Das Papier, **13** (Oct and Dec 1959) 496–503, 592–600

The drop test with lye is a simple way of determining the homogeneity and swelling properties, and hence the suitability, of a pulp. Presence or absence of oxygen and light and the influence of oxidation catalysts over the range 20–60°c. has been investigated. There is a fundamental difference between yellowing at ordinary and at raised temp., determined by the type of cellulose or hemicellulose and by the fines present and not, as previously believed, by the hemicellulose or γ-cellulose content or by copper number. Increase in consistency increased the yellowing in pulps so inclined. Special care is needed when using hardwood pulps. Their tendency to yellow may be offset by addition of a catalyst and working below 45°c. or by addition of carefully controlled amounts of hypochlorite.   R.A.

Distribution of Substituents in Partially Substituted Carboxymethyl Cellulose

I. Croon and C. B. Purves

Svensk Papperstidning, **62** (15 Dec 1959) 876–882

Viscose Cellulose Sulphate

L. E. Akim, T. G. Bamdas, N. A. Mel'chakova, S. L. Talmud, and A. N. Turzhetskaya

Zhur. priklad. khim., **32** (1959) 1324–1332

Under laboratory conditions separating short fibres from an unbleached cellulose sulphate (by washing on sieve No. 65) before bleaching and caustic soda boiling decreases chemical loss of cellulose 36·2–47·5%, the amount of chlorine and caustic soda required by 23·1–26% and 33·3% respectively. In addition the quality of viscose cellulose finally produced is greatly improved. The method is recommended for industrial application.   T.Z.W.

PATENTS

Multiple-coated Offset Paper

Kimberley–Clark   *BP* 824,556

An undercoating containing a finely dispersed mineral pigment, starch and a melamine formaldehyde resin at pH 7·5–9·5 is applied by transfer roll and dried before application of a second coating comprising a pigment in suspension and casein at pH 8–9·5, together with plasticisers, defoaming agents etc. The web is dried, and calendered when the formaldehyde in the undercoating renders the top coating insoluble.   R.A.

Continuous Washing of Regenerated Cellulose Films and the like

DuP   *BP* 822,962

The film is led in a zigzag path in vertical legs, washing liquor being applied to the film at the bottom of each leg so as to form a layer of the liquid on each side of the film. During its passage up some or all of the film is treated with one or more pairs of scrapers, the members of each pair being at different levels and bearing against opposite sides of the film. Part of the liquid removed by a scraper is reapplied to the film above the scraper. By this means film travelling at 100 yd. per min. is readily freed from water-soluble impurities by simple washing with water.   C.O.C.

Antiseptic Paper

Mosinee Paper Mills Co.   *BP* 818,657

Paper coated with 2,2'-methylene-bis-(3,4,6-trichlorophenol)dihydroxydichlorodiphenyl methane, *o*-phenylphenol, *o*-benzyl-*p*-chlorophenol or mixtures of them is antiseptic and has the same strength as the untreated paper.   C.O.C.

Tensile Strength Changes due to Hypochlorite Bleaching (VII p. 131)

XII— LEATHER; FURS; OTHER PROTEIN MATERIALS

PATENTS

Tanning Agent

Boehme Fettchemie   *BP* 825,503

Condensates of high-mol.wt. amines with cyanamide and its derivatives and with oxo compounds used for tanning result in leather of higher flexibility, resistance to water, tenacity and resistance to ageing than that obtained by hitherto known resin tanning agents.   C.O.C.

Tanning with Bivalent Iron Salts

B. Glozic   *BP* 822,997

The skins are treated with an aqueous solution containing a trivalent iron salt and an equivalent quantity of a bichromate. If desired some of the iron salt may be replaced by a trivalent Cr or Al salt. A reducing agent, e.g. $NaHSO_3$, is then added preferably in portions. Compared with leather tanned with iron by previously known processes the leather obtained by the above process has a higher shrinking temperature (about 85°c.) and is plumper, stronger and lighter in colour and more resistant to storage.   C.O.C.

Dressing Leather with Polymer Dispersions in Presence of Zinc Compounds

FBy   *BP* 822,231

Addition of finely divided, active zinc compounds, especially ZnO, to dispersions of polymers containing carboxylic acid groups renders the finish they impart to leather far more stable to hot ironing than those obtained in absence of zinc compounds or obtained in presence of Fe_2O_3, TiO_2 or kaolin.   C.O.C.

Bottoming Agents for Finishing Leather

BASF   *BP* 822,949

Aqueous dispersions of film-forming polymers prepared by use of cationic dispersing agents based on quaternary ammonium compounds and thus being electropositively charged are bottoming agents which impart a well filling sealing coat of uniform gloss even on strongly absorptive leathers.   C.O.C.

Vinyl Polymer Polyepoxy Coating Compositions

Rohm & Haas Co.   *BP* 816,630

Improved adhesion is obtained between a substrate, particularly leather, and polymers applied to it by means of an aqueous vehicle if the polymer contains *t*-amino groups and (1) the aqueous vehicle contains a condensate containing epoxide groups and/or (2) a lacquer-type coating composition having dissolved in it a condensate containing epoxide group is applied on top of the polymers containing *t*-amino groups.   C.O.C.

Waterproofing Leather
Boehme Fettchemie   *BP* 826,065
  Leather, particularly pastel-coloured or white suède and shagreen leather, is impregnated with organic solvent solutions of reaction products of polyvalent metal alcoholates and acid organic derivatives of phosphorous acids of > 5 C.   C.O.C.

XIII— RUBBER; RESINS; PLASTICS

Thirteenth Annual Review of Materials of Construction— Elastomers
B. S. Garvey
    Ind. Eng. Chem., **51** (Sept 1959, Part II) 1167–1171
  A brief review covering recent developments in natural rubber, diene-, butyl-, and silicone-rubbers, fluoropolymers, polyurethanes, vulcanisation and radiation, oxidation and ozonisation, pigments and reinforcement, compounding and theoretical studies. A bibliography (250 references) is appended.   W.K.R.

Thirteenth Annual Review of Materials of Construction— Plastics
R. B. Seymour
    Ind. Eng. Chem., **51** (Sept 1959, Part II) 1204–1212
  Topics discussed include— cellular plastics, industrial applications, plastics resistant to high temperatures, polyolefines, vinyls, polyfluorocarbons, polystyrene, polyacetals, polyesters, and epoxy resins. There is a comprehensive bibliography of recent literature, with 246 references.   W.K.R.

Dichroism of Dyes in Stretched Poly(vinyl Alcohol) Sheets. II— Relationship between the Optical Density Ratio and the Stretch Ratio and an Attempt to Analyse Relative Directions of Absorption Bands
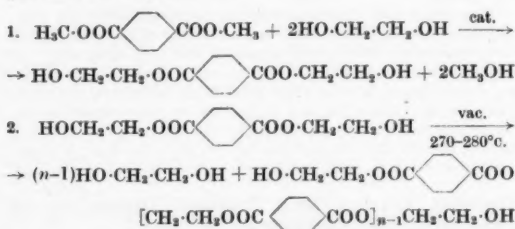Y. Tanikazi
    Bull. Chem. Soc. Japan, **32** (Jan 1959) 75–80

Combination of Re-etherification of Polycondensation during Synthesis of Polyethyleneterephthalate
B. V. Petukhov and A. A. Konkin
    Zhur. priklad. khim., **32** (May 1959) 1171–1173
  The synthesis of polyethyleneterephthalate takes place in two stages—

1. $H_3C \cdot OOC \langle \rangle COO \cdot CH_3 + 2HO \cdot CH_2 \cdot CH_2 \cdot OH \xrightarrow{cat.}$

$\rightarrow HO \cdot CH_2 \cdot CH_2 \cdot OOC \langle \rangle COO \cdot CH_2 \cdot CH_2 \cdot OH + 2CH_3OH$

2. $HOCH_2 \cdot CH_2 \cdot OOC \langle \rangle COO \cdot CH_2 \cdot CH_2 \cdot OH \xrightarrow[270-280^\circ c.]{vac.}$

$\rightarrow (n-1)HO \cdot CH_2 \cdot CH_2 \cdot OH + HO \cdot CH_2 \cdot CH_2 \cdot OOC \langle \rangle COO$

$[CH_2 \cdot CH_2 OOC \langle \rangle COO]_{n-1} CH_2 \cdot CH_2 \cdot OH$

  A good quality polymer was produced using a deficiency of ethylene glycol in the first stage (< 2 mol.). This is explained by the fact that ethylene glycol produced in the second stage of the process continues to react with dimethylterephthalate left over from the first stage.   T.Z.W.

Behaviour of Plastic Materials on Ageing
P. Dubois   *Kunststoffe*, **49** (Nov 1959) 632–645
    German Plastics Digest, **49** (Nov 1959) 40–52
  A review of the problems involved in establishing correlation between methods of determining the effects of ageing. It is doubtful if there is correlation between the results of natural and artificial ageing. 37 references.   C.O.C.

PATENTS

Coated Polyester Film
Winterbottom Book Cloth Co.   *BP* 822,894
  Polyester film is given a firmly adherent coating receptive to clear and legible markings with ink or pencil by treating it with an organic solvent solution of an organic polyisocyanate and treating the resultant coating with a solution of an organic hydrophobic film-forming material. Thus Melinex film (ICI) is coated with Calaroc G (ICI) (17·5 parts by wt.), Calaroc C (10·5), butyl acetate

(7·5), toluene (2·5), benzene (50·5), ethyl acetate (50·5), and 5% Zn resinate in benzene (5·0), dried, heat cured and then coated with low viscosity collodion cotton (9 g.), methylated spirit 64 O. P. (100 c.c.), ethyl acetate (225 c.c.), toluol (100 c.c.), ethylene glycol monoethyl ether (17·5 c.c.), Bedafin 2001 (ICI) (20·0 c.c.), Bedafin 285X (27·5 c.c.), and ground CaSO₄ 50% wt./vol. with acetone (70·0 c.c.), dried, and heat cured. The coated film marks clearly with ink or pencil and the marks can be erased with little or no surface damage.   C.O.C.
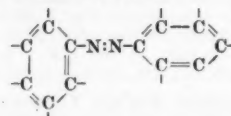
Blends of Styrene Polymers and Rubbery Diene Polymers Coloured with Azo Dyes
Monsanto Chemical Co.   *USP* 2,893,975
  Blends of styrene polymers and rubbery diene polymers containing both alkali metal ions and Ca, Sr or Ba lakes of azo dyes containing the group—

$$-C \langle \rangle C \cdot N{=}N \cdot C \langle \rangle C = C$$

have their colour stabilised by incorporation of ≯ 2% boric acid on the weight of the polymers.
     USP 2,893,975
  Isophthalic and/or terephthalic can replace the boric acid.   C.O.C.

Perforated or Embossed Plastic Sheets
O. Landin   *BP* 818,348
  Plastic either as liquid or paste is applied through a stencil on to a support, to which it does not adhere, to form a film having irregular contours and/or perforations. The film is then solidified and stripped from the support.   C.O.C.

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XIV— ANALYSIS; TESTING; APPARATUS

Viscosimetric Determination of D.P.
E. Treiber, B. Abrahamson, and V. Holta
    Svensk Papperstidning, **62** (15 July 1959) 459–466
  High polymers are characterised by their viscosities at standard conditions, but at times it is desirable to know the chain length which has to be given as the mean average degree of polymerisation (D.P.). The viscosity of colloid solns. is determined by the nature of the colloid (including degree of substitution), concn., temp., nature of solvent, and mean chain length or, according to Eirich, molecular dimension. Data from literature and the authors' experiments with fractionated samples of nitrocellulose in acetone have been reduced to a standard nitrogen content (13·8% N) for calculating the Staudinger constant and more accurate D.P. values. The effect of temp. on η must always be taken into consideration (except for a cellulose/cuoxam system) while the Martin constant (I) and the Houwink exponent can be regarded as being independent of temp., though I may be affected by the state in which the polymer occurs. Within the range 100–2000 D.P. values are determined by $[\eta] = 13 \cdot 6 \times 10^{-3} \times D.P.^{0.948}$. 24 references.   R.A.

The Set of Perlon estimated by Swelling of Cut Ends
H. Modlich   *Melliand Textilber.*, **40** (Aug 1959) 906–911
  The degree of swelling of fibre ends in 325 g. H₂SO₄ per litre under the microscope indicates the degree of set and thus the dry heat or steam treatment temperature of Perlon. Below the optimum temp.— 190°c. for dry heat, 130°c. for steam— extensive swelling occurs, above it none. Practical details, illustrations, and references are extensive, and other testing methods, as well as views on the changes taking place on setting, are reviewed.
     S.M.J.

Colour Measurement Methods Compared
W. Schultze
    Melliand Textilber., **40** (Sept 1959) 1046–1049
  A detailed discussion of principles, fields of application, and advantages and disadvantages of spectrophotometric and tristimulus filter colorimetric methods of colour measurement.   S.M.J.

Mechanism of Pilling
D. Gintis and E. J. Mead

Text. Research J., **29** (July 1959) 578–585

Fabrics subjected to an abrading action initially show increased fuzzing, caused by the abradant pulling exposed fibre sections first into loops then into free ends. Pills formed quickly, when the fuzz density reached a critical level, by the free ends twisting and entangling. As the abrading action continued the pills wore away.

Techniques permitting independent quantitative study of the three stages showed that fuzz formation was dependent on interfibre friction and bending stiffness; that denier, fibre cross-section, and bending stiffness influenced the entanglement stage; and that pill wearoff was determined by abrasion resistance and tenacity.

S.B.D.

An Electrolytic Tank for the Investigation of Fluid Flow Patterns in Yarn Packages
M. J. Denton   *J. Textile Inst.*, **50** (Sept 1959) T 521–527

Following brief consideration of the types of packages used in the wet processing of yarn, use of the electrolytic tank analogue to obtain the flow pattern inside two typical packages is described. The method is applicable to wound packages of any shape, and the electrical analogue constructed for complicated shapes where a mathematical solution would be very difficult and tedious.   C.O.C.

Dye-mixture Analysis with an Electronic Calculating Punch
J. L. F. de Kerf

J. Opt. Soc. Amer., **48** (Dec 1958) 972–597

Calculation of the tristimulus specification of subtractive dye mixtures consists of three parts: calculation of the spectral density of the mixture, conversion to the spectral reflectance or transmittance, and deduction of the tristimulus values and chromaticity co-ordinates. With a standard IBM 604 electronic calculating punch, three runs are needed and the yield is about 24–60 colour points an hour depending on the desired accuracy. With an expanded type, the 604–004, complete calculation can be done in one single run. In this way the yield attained is 60–150 colour points an hour.   C.O.C.

Estimation of Strength of Disperse Dyes
L. M. Golomb

Zhur. priklad. khim., **32** (Aug 1959) 1834–1842

Because of their stability, solutions of acetylated disperse dyes are most suitable for spectrophotometric analyses. The acetates of these dyes are prepared by dissolving 0·010–0·020 g. of a commercial or purified dye in 20 ml. of glacial acetic acid at 20–30°c. and stirring this into 800 c.c. of water at 0°c., containing 4 g./l. of ethylene oxide–alkyl phenol condensate. The soln. is kept until it reaches room temp. before analysis. The sulphates are generally not recommended for this purpose because of decomposition of some of the disperse dyes in H_2SO_4 and the depression of the optical density of their solutions compared with that of the acetate.   T.Z.W.

Determination of Photoactive Properties of Dyes
N. I. Abramova, V. A. Blinov, N. S. Dokunikhin, and V. A. Titkov

Zhur. priklad. khim., **32** (July 1959) 1563–1569

Determination of a Silver No. of a vat-dyed cellulosic material is a very accurate and sensitive method for the estimation of photodegradation of cellulose caused by the dye. The Silver No. is the ml. of 0·01 N-NH_4CNS needed to titrate the Ag precipitated by 1 g. of exposed to sunlight cellulose material tested, from the soln. of Ag hyposulphite complex. The Ag hyposulphite soln. is prepared by gradually adding to a freshly prepared 4% soln. of hyposulphite an equal volume of 1% $AgNO_3$ soln., followed by an equal volume of 4% NaOH soln., with agitation. The test is carried out in a 50 ml. porcelain beaker, containing 25 ml. of this soln. at the boil, to which is added a 0·5 g. sample of the washed cellulosic material to be tested, and boiled for 5 min. longer, filtered and washed with 10% $NaNO_3$ soln. until neutral to phenol-phthalein. The washed textile is transferred to a beaker containing 25 ml. of 20% aq. $NaNO_3$ and brought to 75–80°c. to dissolve all Ag. The beaker content is again filtered, the beaker and the funnel washed well with distilled water. The filtrate and washings are collected together in a

standard flask and titrated against 0·01 N-NH_4CNS using 10 ml. of 10% iron-ammonium alum as indicator.

T.Z.W.

Separation and Identification of Artificial Colours authorised by the Italian Hygiene and Sanitation Commission, 23 Dec. 1957, for use as Food Dyes
R. D. Gori and F. Grandi

Boll. lab. chim. provinciali (Bologna), **9** (1958) 276–286

A mixture of 7 dyes is separated by ether extraction and paper chromatography. They are identified spectrographically. The first chromatographic separation made on circular paper SS 2043/A using as solvent 15 ml. CH_3OH, 30 ml. water and 0·2 g. $MgCl_2·6H_2O$, produces two distinct circular zones after 4 hr. The inner zone contains Azorubine (C.I. Food Red 3) and Amaranth (C.I. Food Red 9), the outer Scarlet GN (C.I. Food Red 2), Fast Red E (C.I. Food Red 4), Victoria Scarlet Red and Ponceau 6R (C.I. Food Red 8). Ether extracts Erythrosine (C.I. Food Red 14) from an aqueous solution of the dyes acidified with acetic acid. The two zones are separated by eluting with water. Using ascending chromatography with each group using SS 2043/A and as solvent 25 ml. H_2O, 25 ml. butyl alcohol and 20 ml. ethyl alcohol, the dyes are completely separated, the respective R_f values being 0·41, 0·12, 0·69, 0·59, 0·25, and 0·10. The E, E/E_{max}, and the characteristic curve for each dye are also given.

C.O.C.

Use of Dye–Quaternary Ammonium Compound Complexes in Identifying Food Dyes
B. Drevon, A. Cier, P. Laroumagne, and J. Lause

Congr. soc. pharm. France, 9°, Clermont-Ferrand (1957) 279–284

Complexes formed from various quaternary ammonium salts with Bromophenol Blue were separated chromatographically on paper impregnated with alumina. The spots were developed with iodine–bismuth reagent. The method can be used for identifying food dyes with a quaternary ammonium salt complex.   C.O.C.

Analysis of Synthetic Food Dyes prescribed in India
B. R. Roy, A. R. Sundarajan, and S. N. Mitra

J. Sci. Ind. Research (India), **18C** (1959) 38–40

Chem. Abs., **53** (10 Oct 1959) 18319

Extraction, chromatography, spectrophotometry, and specific colour reactions are used to separate, identify and determine 11 dyes, prescribed by the Indian government as food colours.   C.O.C.

Fluorimetric Investigations of Fluorescent Brightening Agents
H. Jörder   *Melliand Textilber.*, **40** (Oct 1959) 1190–1194

The Lange photo-electric fluorometer is described and illustrated. Fluorescence of textiles and other substrates, of powders and of solutions, can be measured. Numerous graphs and tables illustrate the increase of fluorescence of Tinopal BV (Gy) with concn. of soln., and with concn. on viscose rayon, and its decrease with increasing temp. of soln. Although fluorescence declines more slowly on Fade-Ometer exposure of very heavily treated fabrics, the greater yellowing of these makes them visually inferior to less heavily treated fabrics. The relative order and intensity of fluorescence of various fluorescent brightening agents is quite different in the solid state, in solution, and on viscose rayon. Any one agent produces very different amounts of fluorescence on different textile substrates.

S.M.J.

Determination of Carotene (C.I. Natural Yellow 26)
F. W. Quackenbush

J. Assoc. Offic. Agr. Chemists, **42** (1959) 528

Chem. Abs., **53** (25 Oct 1959) 18732

Collaborative study of a newly developed method for testing the suitability of a MgO absorbent with FD&C Yellow No. 2 (C.I. Food Yellow 1), used in determining carotene, indicated that further work is necessary. Details of the test are given.   C.O.C.

Photoelectric Colour Difference Meter
R. S. Hunter

J. Opt. Soc. Amer., **48** (Dec 1958) 985–995

The meter has three photo detectors, each with a separate tristimulus filter, and each receiving some of the

light reflected from the sample. Signals from the photo detectors are measured by anologue circuits that give rectangular co-ordinates for surface colours in close correspondence to their positions in uniform colour space.

C.O.C.

Practical Experiences with Coloristic Measurements
A. Brockes

Melliand Textilber., 40 (Sept 1959) 1049–1055

Practical experiences over several years with three filter instruments (Elrepho, Color-Eye) and spectrophotometers (Hardy recording) are summarised. (1) For controlling production, colour difference measurements with filter instruments can be carried out rapidly (4–8 min.) and accurately (errors of measurement of $\frac{1}{4}$–$\frac{1}{8}$ of customary colour tolerances). Best experiences for numerically expressing colour differences were made using MacAdam ellipses. After calculating tristimulus values and chromaticities, the charts of Davidson and Hanlon (*J. Opt. Soc. Amer.*, 45 (1955) 617) are employed to derive differences in hue, ΔC, in MacAdam units from Δx and Δy, and total colour differences from ΔY and ΔC. The greater visual significance of a MacAdam unit in greys than e.g. in deep reds is emphasised. Other colour tolerance formulae proved both more laborious and less accurate. (2) For matching purposes filter instruments do not suffice, because of the problem of metamerism. They can be more rapid than dyers, however, in working out corrections to bring dyeings within tolerance limits of an already accepted match. (3) Standard depths and lightfastness standards require spectrophotometric assessment, owing to insufficient long term reproducibility of filter instruments. Koch's formula (*Melliand Textilber.*, 38 (1957) 73) for deriving depth of colour from tristimulus values has been applied successfully for 3 years, and is related to dye concn. Filter instruments are suitable for grey scale differences. (4) Whiteness and different bleaching treatments are satisfactorily evaluated with filter instruments. (5) Fluorescent brightening agents are satisfactorily compared in an Elrepho filter instrument with a xenon lamp attachment supplying ultraviolet as well as visible radiation, provided the Z filter is sufficiently accurate, and colour selectors or monochromators are operative only between sample and photo-cell, not between light source and sample. Lack of this arrangement renders the Hardy spectrophotometer inaccurate and misleading for fluorescent blues and reds as well as whites.

S.M.J.

Colour Constancy in Shadows
S. M. Newhall, R. W. Burnham, and R. M. Evans

J. Opt. Soc. Amer., 48 (Dec 1958) 976–984

Because colour samples seen as surfaces tend to look much the same under various viewing conditions, they are said to possess colour constancy. Evaluations of colour constancy of 10 colour samples viewed at one time under a standard shadow were made by matching them with a colorimeter whose field was also perceived under the same conditions as the colour sample. In some trials the shadow was present, in some absent, and in others there was no perceived shadow but rather the sample luminance alone was reduced. The data were converted to the Munsell system of renotation. Brunswick-type constancy ratios were formed in terms of Munsell hue, chroma, and value taken separately. The results indicate the constancy of the hue, saturation, and lightness of surface colour perceptions. After weighting the data for each attribute in accordance with an appropriate colour difference formula, an estimate of the combined or over-all colour constancy was obtained.

C.O.C.

Predictions of Shifts in Colour with Change from Daylight to Tungsten Adaptation
R. W. Burnham

J. Opt. Soc. Amer., 48 (March 1959) 254

Charts are given from which predictions for a wide variety of colours may be easily compared with the shifts in colour seen in practice.

C.O.C.

Central Notations for the Revised ISCC-NBS Colour-name Blocks
K. L. Kelly　　*Bur. Stand. J. Res.*, 61 (Nov 1958) 427–431

Nickerson and Newhall published, in 1941, the central notations of the original ISCC–NBS (Inter-Society Color Council–National Bureau of Standards) colour-name

blocks which were used to prepare the soil and rock colour-name charts. In 1955, these blocks were revised to accord more closely with usage in the textile and other fields (NBS Circular 553). The central notations of these revised colour-name blocks have been computed and are now presented in tables. A colour chart showing the central colours of the 267 ISCC–NBS colour-name blocks would serve for rapid determination of the ISCC–NBS colour designation, especially where speed and ease of working are more important than high accuracy. C.O.C.

Spectrophotometric Identification of Small Dye Stains
J. Derkosch

Melliand Textilber., 40 (Oct 1959) 1194–1196

Solvent extracts of stained pillow cases, of blued feathers, and solutions of different basic dyes, alone and in admixture, are examined in a Beckman DU spectrophotometer, and the contaminant is positively identified by means of the curves obtained.

S.M.J.

Resin Distribution in Cotton and Viscose Rayon Investigated with Radio-active Isotopes
H. Enders and R. Zörkendörfer

Melliand Textilber., 40 (Sept. 1959) 1076–1082

A detailed description of the application of autoradiographic techniques to the examination of distribution of C^{14} labelled resin in treated textiles. Results generally tally with those obtained using fluorescent dyes. Distribution is usually uneven in fabric cross-sections, yet regular within an individual fibre.

S.M.J.

Resin Finishing of Cellulose and Suitable Testing Methods— II
K. May, O. Rothe, and L. May

Melliand Textilber., 40 (Sept 1959) 1069–1073

Production control methods for precondensates and finished fabrics are described and very clearly illustrated. Urea– and melamine–formaldehyde resins are mainly considered. Stability of precondensate, in order to prevent excessive condensation leading to surface deposition, is checked by measuring Tyndall effect, viscosity, stiffness of test strips, and pH. Different methods of testing resin distribution on fabrics are described. Dyeing resin with Crystal Ponceau 6R (C.I. Acid Red 44) at pH 2 is preferred for white viscose rayon, and with fluorescent brightening agents or dyes, e.g. Blankophor or Acridine Orange (C.I. Basic Orange 14), for coloureds. Surface depositions become evident microscopically when fibres are in media of similar refractive index, e.g. xylene. Degree of condensation, gravimetric analysis, wash resistance of embossed effects, chlorine retention, and fishy odour are also discussed.

S.M.J.

Dependence of Commercial Determination of Wool Regain on Climatic Considerations
N. F. Roberts　　*J. Textile Inst.*, 50 (Nov 1959) P 678–684

Tentative Textile Standard No. 56. Quantitative Chemical Analysis of Ternary Mixtures of Protein Fibres, Polyamides, and Certain Other Fibres
J. Textile Inst., 50 (Nov 1959) P 692–695

Analysis of Ternary Mixtures containing Wool, Nylon 6,6, and Viscose Rayon
F. F. Elsworth　　*J. Textile Inst.*, 50 (Nov 1959) P 695–696

Experimental results obtained during the development of TTS No. 56 (see preceding abstract).

C.O.C.

Use of Iodine Sorption in Study of Structural Changes of Polyamide Fibres
K. Schwertassek and G. Janáčková

Faserforsch. und Textiltech., 10 (Oct 1959) 472–475

Iodine sorption determinations permit exact measurements of the degree of setting if the wetting temperature and corrections for blank tests are taken into account.

W.R.M.

Microscopic Examination of Stresses in Polyamide Fibrous Material
W. Bobeth and G. Piechottka

Faserforsch. und Textiltech., 10 (Oct 1959) 464–472

Microscopic examination of swelling in sulphuric acid is used to determine changes in set polyamide fibres caused by twisting, bending, scouring, and squeezing. Such examination may be useful in morphological studies or works control.

W.R.M.

Determination of Wet Crease-recovery
W. Ernst and A. Braschler
Textil-Rund., **14** (Sept 1959) 512–514

The strip of fabric is thoroughly wetted, plaited between two steel strips, loaded, and dried. Full details are given and the technique made clear by illustrations.   S.R.C.

Calibration of Brightness Testers
Å. S:son Stenius
Svensk Papperstidning, **62** (30 Nov 1959) 829–833

Introduction of CCA standard 27:58 for measuring the brightness of bleached pulp (*ibid.*, **61** (1958) 336) has made correlation between the Zeiss Elrepho reflectometer and the General Electric Brightness Tester desirable to facilitate maintaining the brightness level specified in *TAPPI* standard T 217 m-48. The CCA Elrepho instrument has been calibrated against the IPC master instrument and it is shown how other Elrepho instruments can be correlated against the CCA master instrument. 10 references.   R.A.

Determination of Specific Gravity of Cellulose
V. T. Sharkov and V. P. Levanova
Zhur. priklad. khim., **32** (Oct 1959) 2357–9

Cellulose in a granular form was dried to absolute dryness at 105°c., wetted with a little ethyl alcohol and washed with CCl_4 for 30 min. It was then transferred to a test tube which was filled with CCl_4 and sealed. The test tube was immersed in a water bath and warmed up until the cellulose remained in suspension, thus attaining the specific wt. of CCl_4 at that temp. The specific wt. found is interpolated to the specific wt. at 20°c. using the equation $d_{20} = d_t + K(t°-20)$ (d_t = sp. wt. at a given temp., K = coeff. of expansion of cellulose = 8×10^{-5}).   T.Z.W.

Estimating Cystine in Wool
A. Schöberl   *Textil Praxis*, **14** (July 1959) 701–708

A critical literature survey (52 references) of experimental methods developed during the last two decades for estimating cystine and cystein. Various workers in this field made use of differing reagents for the characterisation of these sulphur-containing amino-acids. Cystein for instance yields a red product with 1,2-naphthoquinone-4-sulphonic acid, and a blue complex with brucine in presence of K persulphate and 50% H_2SO_4. It can be estimated quantitatively with o-iodo-benzoic acid and phosphotungstic acid (Folin's reagent).   L.A.T.

Spectrophotometric Measurement of Colour in Wool Fabrics
F. G. Lennox   *Text. Research J.*, **29** (Nov 1959) 906–912

A strip of fabric is immersed in a liquid having a refractive index close to that of wool and compared in an ultraviolet spectrophotometer with a similarly immersed uncoloured or bleached strip of the same fabric. This enables detection of sizing and finishing agents present which absorb in the visible or ultraviolet spectra. Wool yellowed by heat or ultraviolet radiation has increased absorption far more in the ultraviolet, especially at 3100–3300 A., than in the visible region above 3900 A.   C.O.C.

Rapid Graphical Computation of Small Colour Differences
F. T. Simon and W. J. Goodwin
Amer. Dyestuff Rep., **47** (1958) 105–112

A method based on the C.I.E. system which permits evaluation of quantitative data that have visual meaning with respect to the colour solid. Control limits may be applied to chromaticity difference, lightness, or over-all colour difference either singly or to all three at once. Furthermore, because of the ease and simplicity of the method, these limits may be maintained on a practical quality control basis.   C.O.C.

Heliostat Insolameter— an Improved Apparatus for Light Exposure Testing
J. Henno and R. Jouhet
Bull. Inst. Text. France, (81) (May 1959) 95–103

An electromechanical azimuthal movement and a cam-controlled declination movement maintain the exposure panel normal to solar radiation. A lux-meter records the total illumination received by the samples. If necessary, the samples can be automatically screened if the intensity of illumination falls below a given value.   J.C.F.

Test for Dimensional Changes in Woven Fabrics in High-temperature Laundering
W. D. Appel
Amer. Dyestuff Rep., **47** (7 April 1958) 213, 220, 240

Results of a study of a test for dimensional changes in woven fabrics in laundering, carried out in the International Organisation for Standardisation, are summarised. The purpose was to provide a basis for agreement on the test to be issued as an I.S.O. Recommendation. Increase in the duration of the test from 60 to 100 min. caused very little increase in shrinkage. Increase in the load of fabric tested at one time from 0·5 to 3 lb./c.ft. had very little consistent effect upon the shrinkage. Dimensional changes in the test applied one or more times and in the same number of commercial launderings were in close agreement. The standard deviation expressing variability between identical specimens of the fabrics tested at different times under the same conditions in the same laboratory was 0·56 in percentage shrinkage: 0·85 between identical specimens in different laboratories.   W.P.M.

New Method of Test for Yarn Slippage in Woven Fabrics
L. S. Veer   *Rayon Revue*, **13** (1) (Nov 1959) 17–27

PATENTS

Evaluating Fluorescent Substances
W. Harrison   BP 822,447

The substance is put on to a substrate, e.g. cloth or paper, and is then subjected to ultraviolet radiation provided by a filament or discharge lamp with an ultraviolet filter. The radiation reflected from the sample is then passed through a second ultraviolet filter of the same kind as the first and is then measured, e.g. by a photoelectric cell connected to a galvanometer. A blank trial with the substrate alone is also made and the result is taken as 100% reflectance or zero absorption value. Thus the greater the fluorescence of the sample the lower is the reflectance value.   C.O.C.

Monitoring the Colour of a Liquid
Proctor & Schwartz   BP 822,027

The strength of a dyebath can be controlled by passing a beam of light having a limited number of frequency bands through a standard and then splitting the beam into two beams of different intensities. The standard is adjusted so that one beam is identical with the transmission through a sample of dye liquor of the correct strength. The other beam is passed through a sample of the dye liquor which is continuously by-passed from and into the main bath. Any deviation from the initial relative light intensities of the two beams after the one has passed through the sample indicates that the bath requires additions to bring it to the correct strength.   C.O.C.

Apparatus for Washing Porous Sheets
National Research Development Corpn.   BP 822,747

Apparatus particularly applicable for washing filter paper used in analytical chromatography.   C.O.C.

Irreversible Temperature Change Colour Indicator
Research Laboratories   USP 2,892,798

A colourless composition which at a chosen temperature in the range $-16°$c. to $0°$c. freezes to a bright yellow or chocolate-coloured ice and which when thawed at a chosen temperature also in the range $-16°$c. to $0°$c. becomes red and retains that colour upon refreezing, comprises a complex or double salt of mercuric and cuprous iodide colloidally dispersed in a solution of an alkali metal iodide. The solution also preferably contains free iodine and a peptising agent, e.g. an alkali metal sulphate.   C.O.C.

Pointer Type Indicating Instruments and Burst Testers
Scientific Instruments (Glasgow)   BP 822,946

Describes a pointer type indicating instrument for indicating the speed of rotation of a slowly rotating member, e.g. the spindle carrying the pointer of a Bourdon pressure gauge. A burst tester is described in which the speed of the ram can be varied so as to give a constant rate of pressure increase to the diaphragm and the material under test.   C.O.C.

XV— MISCELLANEOUS

Optical Properties of Coloured Colloidal Systems. I— Theoretical Studies of the Extinction of Light by Small Sperical Particles
M. Nakagaki

Bull. Chem. Soc. Japan, **31** (Nov 1958) 980–985

Providing U.S. Scientists with Soviet Scientific Information
Office of Scientific Information, National Science Foundation (U.S.) (Aug 1958), pp. 10 + 6 tables

A survey of the journals, etc. published in the Soviet Union, of the U.S. libraries receiving them, and in Table 6 a list of *Russian Scientific Journals Available in English*, with the subscription price of the English translation of each journal and address from which it can be obtained.

C.O.C.

Emery I. Valko
Amer. Dyestuff Rep., **48** (21 Sept 1959) 109–113

An account of the career of the 16th Olney Medallist with a list of his publications and patents.   C.O.C.

History of Textile Education in the Southern Region of the U.S.A.
Alabama Polytechnic Institute
C. L. Adams
Clemson College
G. Gage
Georgia Institute of Technology
J. L. Taylor
North Carolina State College
H. A. Rutherford

Amer. Dyestuff Rep., **48** (21 Sept 1959) 98–104

W. H. Perkin and the Young Chair of Technical Chemistry in the Royal College of Science and Technology, Glasgow
R. Brightman   *Nature*, **182** (30 Aug 1959) 613

Perkin was offered this chair in September 1869 but because of objections by the then professor of chemistry the endowment of the Young Chair was modified and either the offer was not renewed to Perkin under the new conditions or in the meantime he had definitely declined it. Statements that he at any time occupied this chair are incorrect.   C.O.C.

Luminosity and Chromaticity in the Mesopic Range
R. Grigorovici and I. Aricescu-Savopol

J. Opt. Soc. Amer., **48** (Dec 1958) 891–898

Colour-image Synthesis with Two Unorthodox Primaries
A. Karp   *Nature*, **184** (29 Aug 1959), 710–712

An attempt to explain the various phenomena associated with the unorthodox two-colour synthesis of images of natural objects, e.g. that described by Land (J.S.D.C., **75** (Oct 1959) 511).   C.O.C.

Colour Identification as a Function of Extended Practice
R. M. Hanes and M. V. Rhoades

J. Optical Soc. America, **49** (Nov 1959) 1060–4

Use of colour as a coding device has been limited in some important applications because a practical maximum of only about 15 absolutely identifiable colours have been found experimentally. An individual who practiced on Munsell colour chips for about 5 months had continuously improved performance and at the end of the practice period could identify 50 colours with almost absolute accuracy. However, errors increased markedly during three months of no practice immediately following the training period.   C.O.C.

New Visual Phenomenon— the Greenish Yellow Blotch
W. A. Shurcliff

J. Optical Soc. America, **49** (Nov 1959) 1041–8

An observer, viewing only a uniform physical field, finds that his perceptual field suddenly becomes broken up into areas (called pattern and background) that exhibit two very different colours. The pattern arises suddenly and lasts only a few sec. It has an irregular blotchy shape and may be 45° or more wide (becoming smaller in successive experiments and finally remaining absent entirely). The creation of the pattern depends on the spectral energy distribution (*not* the colour) of the physical field. Wavelengths near 570 mμ. and 470 mμ. play crucial and antithetical rôles. The colour of the pattern depends on the spectral distribution of the physical field

being viewed and is neither similar to nor complementary to that of the background or any preceding field. It is suggested that the perceptual field-of-view is governed (as regards yellowness/blueness ratio only) by hundreds of radiation-activated switches arranged in parallel. Each switch is of three-position type and can produce normal yellowness/blueness ratio, extremely high (anomalous ratio), or extremely low (anomalous) ratio. It may be that similar switching plays a part elsewhere in our visual system.   C.O.C.

Fluorescence and Grey Content of Surface Colours
R. M. Evans

J. Optical Soc. America, **49** (Nov 1959) 1049–1059

Investigation of the colours in the Munsell 5R plane and of colours produced in a small aperture in a large white illuminated surround has revealed some interesting and novel relationships. Under these conditions the domain of surface colour perception includes the whole of the range from $V = 0$–10 and $p_c = 0$–1.0 and under some conditions more. For a colour of a given dominant wavelength there is a locus lying wholly within this space along which colours lie that apparently contain no grey. If luminance or purity is increased above a point on this line the sample takes on the appearance characteristic of a fluorescent material. If either is decreased below a point on this line the colour appears to have had a grey component added to the purely chromatic component in increasing amounts until at $p_c = 0$ there is no chromatic component perception of the colour or at low values of V the sample appears black. Above a point somewhat higher than surround luminance, the appearance of fluorescence ceases and the surface mode changes to the illuminant mode, the saturation of the perceived colour decreasing with increasing luminance above this point. A hypothesis to explain the facts is advanced and it is emphasised that more than one *kind* of "brightness" is necessarily involved.   C.O.C.

Calculation of Small Colour Differences
F. L. Wurzburg, A. DiBermardo, and J. R. Cleary

J. Optical Soc. America, **49** (Oct 1959) 974–980

Photoelectric colorimeters used as differential instruments determine the ratios of tristimulus values of similar colorants to a high degree of precision. Hitherto the difficult and lengthy methods of calculating colour coordinate differences from such data have seriously hindered their practical usefulness. Such calculations can be very greatly simplified for small colour differences by using an approximation that becomes increasingly better as the colour difference becomes smaller.   C.O.C.

Influence of Shadow Quality on Colour Appearance
S. M. Newshall, R. W. Burnham, and R. M. Evans

J. Optical Soc. America, **49** (Sept 1959) 909–917

Shadows of skylight quality and of daylight quality were cast upon various samples. The colour of each sample, both shadowed and unshadowed, was matched by adjusting the field of a visual colorimeter. Only skylight shadow evoked any trend in hue and this was towards blue; but both shadows produced systematic losses in saturation and lightness. None of these perceptual changes was as great as the corresponding colorimeter measurement would suggest, i.e. considerable colour constancy was associated with both shadows. The difference in effect between the two shadows was appreciable, as evaluated in Munsell hue, but seemed almost negligible as regards value and chroma.   C.O.C.

Perceived Colour and its Dependence on Focal, Surroundings, and Preceding Stimulus Variables
D. Jameson and L. M. Hurvich

J. Optical Soc. America, **49** (Sept 1959) 890–8

Some Multivariate Statistical Techniques used in Colour Matching Data
J. E. Jackson   *J. Optical Soc. America*, **49**, 585–592

PATENT

Transferring Cut Fur to a Backing
J. Vandeweghe   *BP* 822,967

A temporary distortable binding agent is applied to the hair of a pelt. The skin is then removed leaving the hair in an orderly pliable and flexible assembly which can be stretched or compacted to obtain any desired density of hair. Finally the desired backing is placed upon the assembly and bonded to it after which the binding agent is removed from the hair.   C.O.C.

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